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Investigation of the Phosphorus–Carbon Bond Lengths in Aromatic Phosphines. II. Crystal and Molecular Structures of Tri-*m*-tolylphosphine, Tri-*m*-tolylphosphine Sulphide and Tri-*m*-tolylphosphine Selenide

By T. STANLEY CAMERON*

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

KEITH D. HOWLETT

Crystallography Laboratory, 9 Parks Road, Oxford OX1 3QR, England

AND KENNETH MILLER

*University of Ulster, Coleraine, N. Ireland*

Of the title compounds, the sulphide and selenide are isomorphous. The differences in the P–C bond lengths appear to be determined by the oxidation state of the P and by steric hindrance and crystal-packing forces, but not by any extension of the π system of the aromatic group to the P atom. [Tri-*m*-tolylphosphine: orthorhombic, *Pbca*, $a = 10.50$ (1), $b = 20.51$ (2), $c = 15.98$ (1) Å; tri-*m*-tolylphosphine sulphide: orthorhombic, *Pbca*, $a = 29.31$ (3), $b = 10.29$ (1), $c = 11.96$ (1) Å; tri-*m*-tolylphosphine selenide: orthorhombic, *Pbca*, $a = 29.51$ (4), $b = 10.46$ (2), $c = 12.38$ (2) Å.]

Introduction

In order to investigate the factors that influence the variation in P–C bond lengths of aromatic phosphines the structures of tri-*o*-, tri-*m*- and tri-*p*-tolylphosphine, -phosphine oxide, -phosphine sulphide and -phosphine selenide [$(CH_3C_6H_4)_3PX$, X = lone pair, O, S, Se] have been determined. The structures of the tri-*o*-tolyl compounds have already been discussed (Cameron & Dahlén, 1975); reported here are the structures of the tri-*m*-tolyl derivatives (Cameron, Howlett, Shaw & Woods, 1973) [(I), (II), and (III)].

(I)   (II)   (III)

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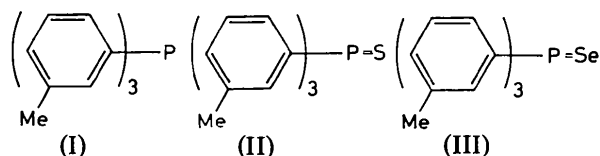
* To whom correspondence should be addressed.

Experimental

The crystals were provided by Dr M. Woods, Birkbeck College, London.

Crystal data

(I) Tri-m-tolylphosphine, $C_{21}H_{21}P$, $M_r = 304$, orthorhombic, $a = 10.50$ (1), $b = 20.51$ (2), $c = 15.98$ (1) Å, $D_m = 1.177$, $Z = 8$, $D_c = 1.175$ g cm^{-3}. Space group $Pbca$, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 13.37$ cm^{-1}.

(II) Tri-m-tolylphosphine sulphide, $C_{21}H_{21}PS$, $M_r = 336$, orthorhombic, $a = 29.31$ (3), $b = 10.29$ (1), $c = 11.96$ (1) Å, $D_m = 1.18$, $Z = 8$, $D_c = 1.24$ g cm^{-3}. Space group $Pbca$, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 2.64$ cm^{-1}.

(III) Tri-m-tolylphosphine selenide,* $C_{21}H_{21}PSe$, $M_r = 383$, orthorhombic, $a = 29.51$ (4), $b = 10.46$ (2), $c = 12.38$ (2) Å, $D_m = 1.331$, $Z = 8$, $D_c = 1.332$ g cm^{-3}. Space group $Pbca$, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å,

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* Tri-m-tolylphosphine oxide is thought to be isomorphous with (II) and (III) [cell dimensions: $a = 29.35$ (1), $b = 10.282$ (5), $c = 12.015$ (5) Å].

Table 1. *Atomic coordinates* ($\times 10^4$)

	x	y	z
(I) Tri-m-tolylphosphine			
P(1)	2327 (1)	4365 (1)	4931 (1)
C(11)	979 (7)	3810 (4)	5108 (4)
C(12)	1057 (8)	3240 (4)	5553 (4)
C(13)	−17 (9)	2841 (5)	5633 (5)
C(14)	−1169 (8)	3012 (4)	5241 (4)
C(15)	−1246 (7)	3587 (4)	4790 (4)
C(16)	−179 (7)	3981 (4)	4724 (4)
C(17)	−2509 (8)	3788 (5)	4378 (5)
C(21)	3407 (7)	4108 (4)	5775 (4)
C(22)	4468 (8)	3703 (4)	5656 (4)
C(23)	5263 (9)	3562 (5)	6337 (5)
C(24)	4997 (9)	3794 (5)	7108 (5)
C(25)	3937 (8)	4194 (4)	7253 (4)
C(26)	3161 (8)	4357 (4)	6575 (4)
C(27)	3636 (10)	4467 (5)	8122 (5)
C(31)	3081 (7)	4011 (4)	4005 (4)
C(32)	4160 (8)	4318 (5)	3675 (5)
C(33)	4770 (9)	4082 (5)	2993 (5)
C(34)	4303 (8)	3531 (4)	2570 (4)
C(35)	3221 (8)	3220 (4)	2890 (4)
C(36)	2641 (7)	3453 (4)	3594 (4)
C(37)	2735 (11)	2607 (6)	2445 (6)
H(12)	1887	3117	5814
H(13)	43	2433	5974
H(14)	−1934	2726	5288
H(16)	−246	4393	4394
H(22)	4652	3516	5091
H(23)	6047	3286	6271
H(24)	5594	3667	7571
H(26)	2435	4661	6666
H(32)	4520	4720	3938
H(33)	5553	4309	2802
H(34)	4736	3873	2046
H(36)	1879	3214	3810

Table 1 (*cont.*)

	x	y	z
(II) Tri-m-tolylphosphine sulphide			
P(1)	1226 (1)	1576 (2)	3043 (2)
S(1)	1125 (1)	840 (3)	4513 (2)
C(1)	1744 (3)	2564 (10)	2976 (10)
C(2)	2092 (3)	2268 (13)	3720 (12)
C(3)	2499 (4)	2983 (12)	3632 (14)
C(4)	2550 (4)	3914 (13)	2864 (12)
C(5)	2208 (3)	4258 (9)	2173 (10)
C(6)	1795 (3)	3516 (9)	2225 (9)
C(7)	2252 (5)	5278 (14)	1301 (15)
C(11)	765 (2)	2645 (8)	2623 (9)
C(12)	657 (3)	3652 (10)	3335 (12)
C(13)	302 (4)	4478 (12)	3068 (13)
C(14)	51 (4)	4287 (11)	2137 (12)
C(15)	144 (3)	3259 (12)	1412 (11)
C(16)	513 (3)	2431 (9)	1693 (8)
C(17)	−130 (4)	3050 (15)	360 (13)
C(21)	1292 (3)	342 (9)	1984 (10)
C(22)	1160 (3)	−896 (9)	2247 (10)
C(23)	1195 (4)	−1896 (11)	1477 (11)
C(24)	1373 (3)	−1605 (12)	440 (12)
C(25)	1508 (4)	−376 (11)	157 (11)
C(26)	1459 (3)	614 (11)	928 (10)
C(27)	1034 (5)	−3269 (13)	1795 (14)
(III) Tri-m-tolylphosphine selenide			
P(1)	1231 (2)	1593 (6)	3007 (6)
Se(1)	1113 (1)	799 (3)	4547 (3)
C(1)	1754 (8)	2582 (32)	2978 (21)
C(2)	2095 (8)	2248 (34)	2725 (26)
C(3)	2492 (12)	2970 (31)	2623 (29)
C(4)	2541 (10)	3986 (32)	2823 (26)
C(5)	2189 (9)	4310 (27)	2068 (27)
C(6)	1780 (9)	3545 (24)	2170 (22)
C(7)	2250 (15)	5291 (37)	1273 (35)
C(11)	775 (7)	2550 (21)	2568 (20)
C(12)	657 (9)	3722 (21)	3241 (24)
C(13)	305 (9)	4455 (30)	2985 (28)
C(14)	56 (10)	4252 (28)	2076 (27)
C(15)	143 (8)	3192 (27)	3632 (24)
C(16)	520 (7)	2300 (6)	1630 (21)
C(17)	−112 (10)	2923 (36)	334 (28)
C(21)	1308 (8)	376 (23)	1956 (22)
C(22)	1182 (8)	−876 (25)	2226 (21)
C(23)	1194 (9)	−1847 (30)	1456 (23)
C(24)	1365 (9)	−1611 (28)	388 (24)
C(25)	1509 (9)	−380 (26)	169 (23)
C(26)	1453 (8)	617 (21)	947 (18)
C(27)	1027 (12)	−3209 (29)	1747 (28)

$\mu = 37.09$ cm^{-1}. All three crystals form needles with an approximately square cross-section; thin well-formed crystals were selected for each compound with cross-section side lengths of 0.4 [(I) and (II)] and 0.3 mm (III). The crystal of (III) was close to the optimum thickness (0.5 mm), but no absorption correction was applied since the structure was determined to confirm that (II) and (III) were isomorphous. Absorption corrections were not thought necessary for (I) and (II).

The reflection data from (I) and (III) were estimated visually from equi-inclination Weissenberg photographs and those of (II) were measured with a Hilger & Watts

linear diffractometer for 0–8kl, hk0–11 and h0–10l; 1716, 1590 (with $I > 3\sigma$) and 1493 independent reflections were significantly above background for (I), (II) and (III) respectively.

The structures were determined by the direct method (symbolic addition) and refined by full-matrix least squares [$\Sigma w(\Delta F)^2$ = minimum] for compound (II) and by block-diagonal least squares for the other two compounds. The individual weights (Mills & Rollett, 1961) for each reflection were given by: $w = \{1 + [(|F_o| - P_1)/P_2]^2\}^{-1}$, where P_1 and P_2 were 40 and 60 (I), 47 and 70 (II), and 60 and 100 (III). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and were corrected for the real part of the anomalous dispersion. Individual anisotropic temperature factors on all atoms were used in the final cycles of refinements and the H atoms could only be located for (I) in the difference Fourier series. Final convergence for those reflections significantly greater than background was at conventional R values of 0·10, 0·10 and 0·11 for compounds (I), (II) and (III) respectively, where the difference Fourier series showed no unusual features.

The atomic coordinates are given in Table 1 and the interbond angles for the three compounds in Table 2. The individual molecule for each compound is shown in Fig. 1. Figs. 2 and 3 give stereoscopic projections of the phosphine and phosphine sulphide/selenide unit cells and Fig. 4 displays the interatomic distances.*

Table 2. Interbond angles (°)

	(I)		(I)
C(11)–P(1)–C(21)	100·6 (3)	C(21)–C(22)–C(23)	119·4 (7)
C(11)–P(1)–C(31)	102·2 (3)	C(22)–C(23)–C(24)	120·8 (8)
C(21)–P(1)–C(31)	102·2 (3)	C(23)–C(24)–C(25)	121·4 (8)
P(1)–C(11)–C(12)	124·2 (5)	C(24)–C(25)–C(26)	118·4 (7)
P(1)–C(11)–C(16)	116·3 (5)	C(24)–C(25)–C(27)	121·8 (7)
C(12)–C(11)–C(16)	119·4 (6)	C(26)–C(25)–C(27)	119·8 (7)
C(11)–C(12)–C(13)	119·8 (7)	C(21)–C(26)–C(25)	120·9 (7)
C(12)–C(13)–C(14)	120·4 (7)	P(1)–C(31)–C(32)	118·4 (6)
C(13)–C(14)–C(15)	119·6 (7)	P(1)–C(31)–C(36)	124·2 (5)
C(14)–C(15)–C(16)	119·3 (7)	P(32)–C(31)–C(36)	117·3 (6)
C(14)–C(15)–C(17)	120·2 (7)	C(31)–C(32)–C(33)	121·6 (8)
C(16)–C(15)–C(17)	120·5 (6)	C(32)–C(33)–C(34)	120·7 (8)
C(11)–C(16)–C(15)	121·3 (6)	C(33)–C(34)–C(35)	118·3 (8)
P(1)–C(21)–C(22)	124·1 (7)	C(34)–C(35)–C(36)	120·2 (7)
P(1)–C(21)–C(26)	116·8 (6)	C(34)–C(35)–C(37)	118·3 (7)
C(22)–C(21)–C(26)	119·1 (7)	C(36)–C(35)–C(37)	121·4 (7)
		C(31)–C(36)–C(35)	121·3 (7)

	(II)	(III)
*S(1)–P(1)–C(1)	112·6 (4)	112·0 (7)
S(1)–P(1)–C(11)	112·0 (4)	112·1 (7)
S(1)–P(1)–C(21)	112·2 (4)	112·9 (7)
C(1)–P(1)–C(11)	105·7 (5)	108 (1)
C(11)–P(1)–C(21)	105·8 (5)	106 (1)
C(11)–P(1)–C(21)	108·2 (5)	106 (1)
P(1)–C(1)–C(2)	117·4 (9)	116 (1)
P(1)–C(1)–C(6)	121·9 (8)	117 (1)
C(2)–C(1)–C(6)	120·7 (10)	126 (2)
C(1)–C(2)–C(3)	117·5 (12)	113 (2)
C(2)–C(3)–C(4)	121·5 (13)	122 (2)
C(3)–C(4)–C(5)	121·8 (12)	123 (2)
C(4)–C(5)–C(6)	117·6 (10)	114 (1)
C(4)–C(5)–C(7)	123·6 (11)	122 (2)
C(6)–C(5)–C(7)	118·7 (10)	124 (2)
C(1)–C(6)–C(5)	120·8 (9)	119 (2)
P(1)–C(11)–C(12)	117·1 (8)	118 (1)
P(1)–C(11)–C(16)	122·4 (7)	124 (1)
C(12)–C(11)–C(16)	120·4 (9)	119 (2)
C(11)–C(12)–C(13)	119·5 (12)	121 (1)
C(12)–C(13)–C(14)	120·9 (13)	122 (2)
C(13)–C(14)–C(15)	121·1 (11)	122 (2)
C(14)–C(15)–C(16)	117·3 (11)	119 (1)
C(14)–C(15)–C(17)	121·4 (11)	125 (2)
C(16)–C(15)–C(17)	121·3 (11)	116 (2)
C(11)–C(16)–C(15)	120·9 (10)	118 (1)
P(1)–C(21)–C(22)	117·7 (9)	117 (2)
P(1)–C(21)–C(26)	122·4 (8)	125 (1)
C(22)–C(21)–C(26)	119·9 (11)	119 (2)
C(21)–C(22)–C(23)	121·2 (11)	121 (1)
C(22)–C(23)–C(24)	117·7 (11)	121 (2)
C(22)–C(23)–C(27)	119·7 (12)	120 (2)
C(24)–C(23)–C(27)	122·6 (12)	119 (2)
C(23)–C(24)–C(25)	122·2 (13)	117 (2)
C(24)–C(25)–C(26)	119·2 (12)	120 (2)
C(21)–C(26)–C(25)	119·8 (11)	122 (1)

* Se(1) for (III).

Results and discussion

The dimensions reported here for the three structures must be treated with some caution since the use of visually estimated data without absorption corrections for compounds (I) and (III), the inability to locate the H atoms in (II) and (III) and the lack of thermal-parameter corrections, all introduce systematic errors, while the block-diagonal-refinement procedure has probably underestimated the values of the e.s.d.'s.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33244 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
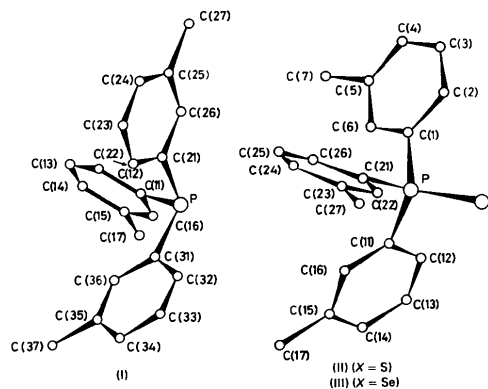

Fig. 1. Individual molecules of (I), (II), and (III). (I) is projected along a, (II) and (III) are projected along b.

The structures of tri-*m*-tolylphosphine oxide, sulphide and selenide are isomorphous and only those of the sulphide and selenide have been fully determined. Of these, the structure of the sulphide (II), determined from data collected by a diffractometer, is the more accurate and in the discussion that follows it will largely be used to represent all three compounds.

The tri-*m*-tolylphosphine molecule (I) adopts the 'paddle' configuration, but in this case two of the methyl groups are on the same side of the molecules as the lone pair and one is on the other side. This is the reverse of the sulphide (Fig. 1). In the unit cell the molecules pack in stacks along **b** where pairs of molecules have the lone-pair electrons adjacent, with those of one molecule fitting between two tolyl groups of the other. The tolyl groups pack together mainly in the edge-to-face arrangement (Fig. 2).

In the molecule of the sulphide, the three phenyl groups have the familiar 'paddle' arrangement but the three *meta* methyl groups do not adopt similar conformations. Two are towards the side of the molecule opposite to the S atom, the third is on the same side. In the crystal the molecules pack together in stacks along **c**; adjacent molecules are in similar orientations but with the P–S bond inclined alternately 15° to either side of the stack axis (Fig. 3). Within the stacks, therefore, the S atoms fit between two tolyl groups of the molecule above. The molecules themselves are so arranged that the tolyl groups also fit between those of the molecule below with the edges of the phenyl rings of the upper molecule making the close contact to the faces of those below.

The different conformations of the tolyl groups in the phosphine and the phosphine sulphide are probably required for efficient packing of the molecules in the crystal. Certainly it is clear from Figs. 2 and 3 that the packing observed for each compound would not be possible if the conformation were reversed, and, since in

solution the methyl proton signals in the ^{1}H NMR spectra are all equivalent (Shaw, 1972), it would appear that in solution there is free rotation around the P–C bond.

Within the molecules the C–C bond lengths are not significantly different from the expected values; mean C–C (phenyl) are 1·390, 1·379 and 1·417 Å and mean C–Me are 1·533, 1·513 and 1·497 Å, for (I), (II) and (III) respectively. The mean C–P–C angles of 101·7 (2), 106·6 (3) and 106·6 (7)° follow the trend predicted by Gillespie & Nyholm (1957) and are very similar to those of 102·6 (1), 106·1 (2) and 106·7 (2)° observed in the tri-*o*-tolyl derivatives (Cameron & Dahlén, 1975). The P=S and P=Se bond lengths [1·936 (5) and 2·109 (7) Å] are similarly unexceptional and compare with 1·947 (5) and 2·116 (5) Å in the corresponding tri-*o* compounds.
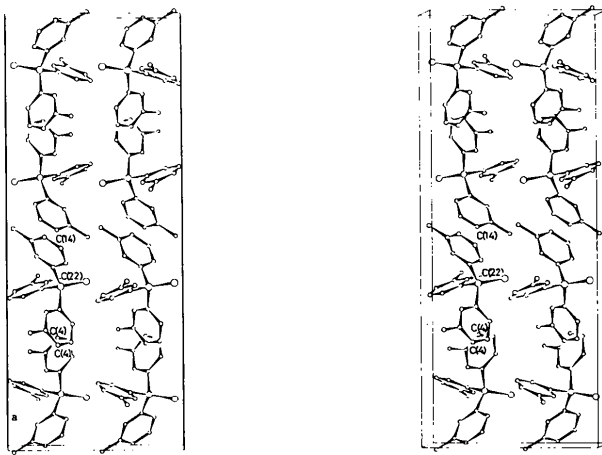

Fig. 3. Stereoscopic projection of the unit cells of tri-*m*-tolylphosphine sulphide and tri-*m*-tolylphosphine selenide viewed along **b**.
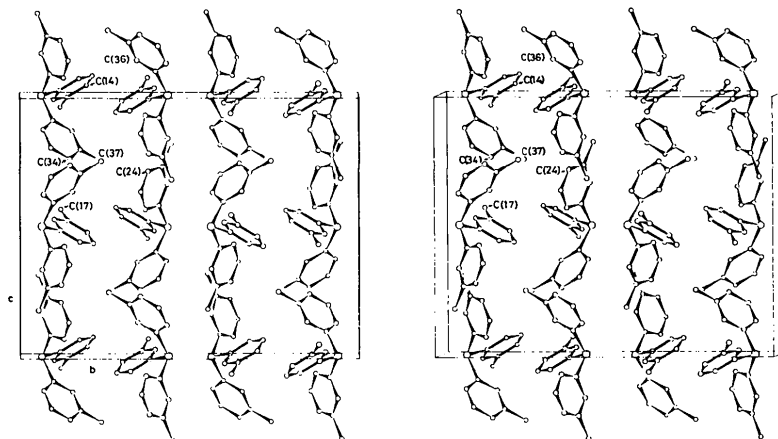

Fig. 2. Stereoscopic projection of the unit cell of tri-*m*-tolylphosphine viewed along **a**.

Table 3. P—C *bond lengths* (Å), *torsional angles* (°) *between* P—X *and* C—C *about the* P—C *bond, and the shortest contact* (Å) *to the phenyl atoms para to the* P—C *bond*

	P—C bond length	Torsional angle	Intermolecular contact
Tri-*m*-tolylphosphine			
P(1)—C(11)	1·838 (8)	35	3·75
P(1)—C(21)	1·838 (7)	47	3·77
P(1)—C(31)	1·829 (7)	53	3·69
Tri-*m*-tolylphosphine sulphide			
P(1)—C(1)	1·830 (10)	27	3·75*
P(1)—C(11)	1·814 (9)	55	3·63
P(1)—C(21)	1·804 (11)	15	>4·0
Tri-*m*-tolylphosphine selenide			
P(1)—C(1)	1·86 (2)	27	3·75*
P(1)—C(11)	1·77 (2)	63	3·76
P(1)—C(21)	1·83 (2)	11	>4·0

* Plane-to-plane contact.

The P—C interatomic distances are in the ranges 1·829–1·838 Å [mean 1·835 (5) Å], 1·804–1·830 Å [mean 1·816 (7) Å] and 1·767–1·858 Å [mean 1·819 (15) Å], for compounds (I), (II) and (III). Table 3 gives the individual P—C bond lengths for each compound with the torsional angle between the axis of the P=X bond or lone-pair orbital and the plane of the phenyl about the corresponding P—C bond. In the phosphine (I) the three shortest intermolecular contacts to the C atom *para* to the P—C bond are C(14)···C(36), C(24)···C(37) and C(34)···C(17) (Fig. 1). Each is about 3·7–3·8 Å and the steric interaction in each case would tend to force one tolyl group towards the other two rather than to shorten the P—C bond. This may be the reason why the mean C—P—C angle of 101·7° has slightly contracted from the mean value of 102·6° in the *o*-tolyl compound where one might have expected the angle to expand when the *ortho* methyl groups were replaced by the less sterically hindering *meta* groups.

With the sulphide and selenide, (II) and (III), the P—C bond lengths occur with a wider spread of values than in compound (I), though the long and short P—C bonds in compounds (II) and (III) correspond. The difference between these bond lengths in each compound is, on e.s.d. evidence alone, barely significant but the correspondence between the lengths in the two isomorphous structures increases the significance a little. There is a reasonably short intermolecular contact between C(14)···C(22)' of 3·63 Å in (II) (Fig. 3). The steric effect of this is principally a force acting down the P(1)—C(11) bond tending to shorten it and this P—C bond length is one of the short ones. The other short contacts in the molecule are a plane-to-plane contact between C(4) and C(4)' and a methyl contact approxi-
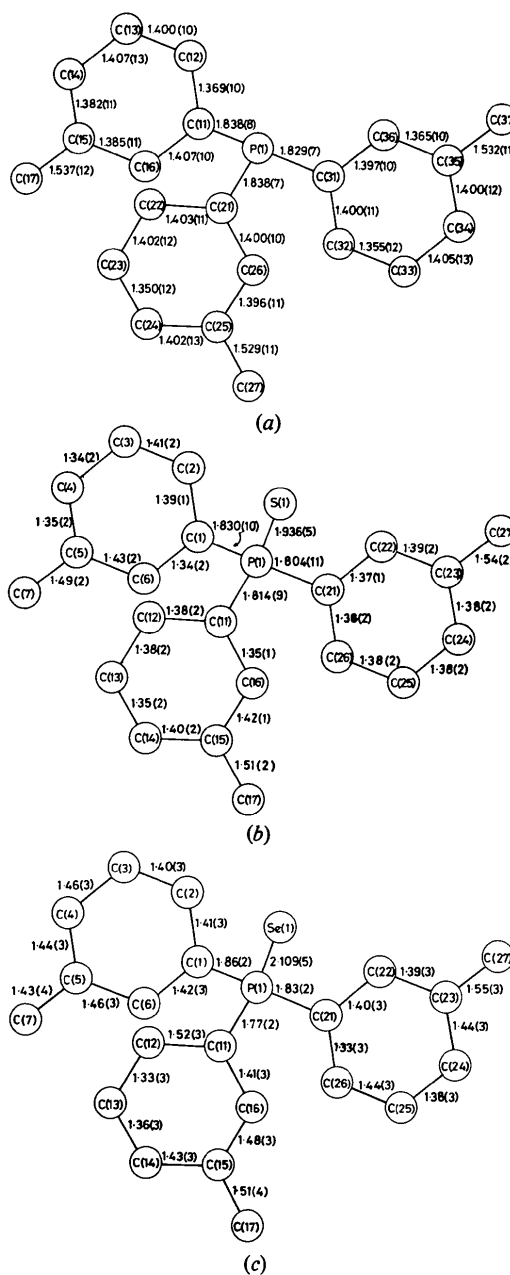

Fig. 4. Interatomic distances (Å) for (a) tri-*m*-tolylphosphine, (b) tri-*m*-tolylphosphine sulphide and (c) tri-*m*-tolylphosphine selenide.

mately perpendicular to the phenyl plane between C(27) and C(13)'. From Table 3 the torsion-angle differences between the group with the long and those with the short P—C bond lengths are approximately −15 and +30° and it would seem, therefore, that the torsion angle has little influence on this bond length, and presumably there is no significant π delocalization from the tolyl ring to the P atom.

The mean P–C bond lengths for the sulphide and selenide are almost exactly the same (~1·812 Å) but are noticeably longer in the phosphine (1·835 Å). The lengths do not vary significantly from those observed in the o-tolyl derivatives and it would seem, therefore, that the position of substitution of the methyl group has no direct effect upon them. The length of the P–C bonds seems to be influenced by two factors only: the valence state of the P atom and, for individual bond lengths, the degree of intermolecular steric hindrance.

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Structures of Polyfluoroaromatic Compounds.
II.* Crystal Structure of 2,3,5,6-Tetrafluorobiphenyl

By N. GOODHAND AND T. A. HAMOR†

Department of Chemistry, University of Birmingham, Birmingham B15 2TT, England

$C_{12}H_6F_4$ is monoclinic, space group $P2_1/c$, with $a = 12.92$ (1), $b = 5.91$ (1), $c = 12.90$ (1) Å, $\beta = 104.22$ (5)°, $Z = 4$. The structure was refined to $R = 4.35\%$ for 904 counter amplitudes. The angle between the phenyl rings is 57.9° and the inter-ring bond length is 1.492 Å (uncorrected for thermal libration). Estimated standard deviations average 0.005 Å for bond lengths and 0.3° for bond angles.

Introduction

The structure of biphenyl has been investigated by X-ray crystallography, gas-phase electron diffraction and spectroscopic techniques (see references cited in part I of this series). We have now determined the crystal structure of 2,3,5,6-tetrafluorobiphenyl (Chaudhry & Stephens, 1963) as part of a continuing study of highly fluorinated molecules.

Experimental

Suitable crystals were obtained from aqueous methanol. A crystal 0.6 × 0.3 × 0.2 mm was sealed in a Pantak capillary tube and aligned about y. Initial photographs determined the space group and approximate cell dimensions. Final cell dimensions and intensities

were measured with a Stoe computer-controlled two-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The diffractometer was operated in the ω-scan mode (Goodhand & Hamor, 1978) with a scan rate of 0.6° min⁻¹ and 30 s background counts at each end of the scan. Four zero-layer reflexions were remeasured after each layer of data collection to check the stability of the system. Of 2492 unique reflexions scanned within the range $0.1 < \sin\theta/\lambda < 0.65$ Å⁻¹, 904 with $I > 2.5\sigma(I)$ were considered to be observed and were used in the analysis.

Crystal data

$C_{12}H_6F_4$, $M_r = 226.2$, monoclinic, $a = 12.92$ (1), $b = 5.91$ (1), $c = 12.90$ (1) Å, $\beta = 104.22$ (5)°, $U = 955$ Å³, $D_c = 1.57$ g cm⁻³, $Z = 4$, $F(000) = 456$; systematic absences: $0k0$, k odd; $h0l$, l odd; space group $P2_1/c$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å; μ(Mo $K\alpha) = 0.99$ cm⁻¹.

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* Part I: Hamor & Hamor (1978).
† To whom correspondence should be addressed.