Table 4. *Dimensions* (Å) *of pentalene frameworks*

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
a(S—N)	1·959	1·927	2·034[A]	1·909	1·904	1·925	2·321[D]	2·350[D]
b(S—C)	1·717	1·717	1·852[B]	1·705	1·764	1·742	1·784	1·789
c(N—C)	1·328	1·324	1·294	1·300	1·316	1·328	1·694[E]	1·711[E]
d(N—C)	1·437	1·438	1·432	1·423	1·354	1·363[C]	1·328	1·340
e(N—C)	1·324	1·333	1·329	1·333	1·336	1·398[C]	1·336	1·329

A: Se—N *B*: Se—C *C*: C—C *D*: S—S *E*: S—C

Crystal structures. The crystal structures are shown in Fig. 2. In the structure of (I) an intermolecular distance shorter than that of the van der Waals contact is 2·924 (9) Å of $O(2)\cdots C(3^{i})$ [(i): $\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$]. Two independent molecules, *A* and *B*, of (II) are related by a pseudo center of symmetry. Intermolecular distances only slightly shorter than the van der Waals contact are 3·065 (7) Å in $O(2A)\cdots C(8B^{i})$ [(i): x, $y+1$, z] and 3·050 (7) Å in $O(5A)\cdots C(8A^{ii})$ [(ii): $-x$, $1-y$, $-z$]. The structure of (III) is isomorphous with that of (IV). There are no intermolecular distances shorter than the van der Waals distances. The packing mode of (III) and (IV) is quite different from that of (II) as shown in Fig. 2.

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Structure of Tris(2,6-dimethoxyphenyl)phosphine

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Abstract. $C_{24}H_{27}O_6P$, M_r = 442·45, *Pbca*, orthorhombic, a = 7·615 (3), b = 20·087 (8), c = 29·447 (10) Å, V = 4507 Å^3, Z = 8, D_x = 1·304 g cm^{-3}, Cu $K\alpha$, λ = 1·54184 Å, μ = 13·79 cm^{-1}, $F(000)$ = 1872, T = 295 K, R = 0·0568 for 3067 unique reflections. P—C bond lengths (av. = 1·844 Å) are slightly elongated relative to those of triphenylphosphine (av. = 1·828 Å). C—P—C bond angles (av. = 104·4°) are only slightly larger than those of triphenylphosphine (av. = 103·0°). The plane of one aromatic ring is roughly perpendicular to the plane defined by the three C atoms bound to the P atom while the other two rings are tilted.

Introduction. Tris(2,6-dimethoxyphenyl)phosphine, (1), has been reported (Wada & Higashizaki, 1984) to have very high basicity (p$K_a \simeq 10$) as compared to ordinary triarylphosphines [*e.g.* Ph_3P, pK_a 2·7 (Henderson & Streuli, 1960)]. In addition to enhanced Brønsted basicity, (1) possesses very strong Lewis basicity. It reacts with CH_2Cl_2 rapidly at room temperature to give the chloromethylphosphonium chloride; by contrast triphenylphosphine may be kept in CH_2Cl_2 for extended periods. Wada & Higashizaki (1984) referred to the phosphine's aryl groups as 'bulky' and suggested that, in part, its unusual reactivity might be attributable to *B*-strain. Thus it was of interest to determine the structure of (1).

Experimental. Colorless prisms, 0·25 × 0·20 × 0·20 mm, were obtained by slow evaporation of an

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
P(1)	1251 (1)	4082 (1)	1301 (1)	40 (1)
C(1)	−529 (4)	4694 (2)	1354 (1)	43 (1)
C(2)	−2224 (4)	4600 (2)	1176 (1)	47 (1)
C(3)	−3550 (5)	5061 (2)	1237 (1)	64 (1)
C(4)	−3180 (7)	5637 (2)	1463 (2)	80 (2)
C(5)	−1576 (7)	5766 (2)	1623 (2)	80 (2)
C(6)	−233 (5)	5299 (2)	1570 (1)	64 (1)
O(1)	−2470 (3)	4016 (1)	953 (1)	60 (1)
C(7)	−4098 (5)	3887 (2)	750 (1)	69 (1)
O(2)	1428 (4)	5472 (2)	1705 (1)	92 (1)
C(8)	1882 (8)	5298 (3)	2136 (2)	124 (3)
C(9)	1147 (4)	3933 (2)	685 (1)	40 (1)
C(10)	602 (4)	3368 (2)	449 (1)	47 (1)
C(11)	712 (5)	3336 (2)	−23 (1)	65 (1)
C(12)	1347 (5)	3867 (2)	−264 (1)	70 (2)
C(13)	1877 (5)	4437 (2)	−50 (1)	64 (1)
C(14)	1782 (4)	4471 (2)	423 (1)	48 (1)
O(3)	−91 (4)	2864 (1)	697 (1)	62 (1)
C(15)	−126 (8)	2230 (2)	519 (2)	97 (2)
O(4)	2265 (3)	5010 (1)	670 (1)	61 (1)
C(16)	2945 (5)	5575 (2)	443 (2)	73 (2)
C(17)	484 (4)	3312 (2)	1586 (1)	46 (1)
C(18)	−950 (5)	3247 (2)	1877 (1)	57 (1)
C(19)	−1253 (6)	2654 (2)	2108 (1)	71 (2)
C(20)	−128 (8)	2137 (2)	2064 (2)	83 (2)
C(21)	1341 (6)	2181 (2)	1799 (2)	71 (2)
C(22)	1642 (5)	2774 (2)	1563 (1)	55 (1)
O(5)	−1976 (4)	3789 (2)	1936 (1)	79 (1)
C(23)	−3648 (6)	3726 (3)	2135 (2)	92 (2)
O(6)	3090 (4)	2866 (1)	1293 (1)	66 (1)
C(24)	4366 (7)	2369 (2)	1281 (2)	97 (2)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

P(1)—C(1)	1·836 (3)	P(1)—C(9)	1·842 (3)
P(1)—C(17)	1·855 (3)	C(1)—C(2)	1·406 (5)
C(1)—C(6)	1·392 (5)	C(2)—C(3)	1·382 (5)
C(2)—O(1)	1·357 (4)	C(3)—C(4)	1·364 (6)
C(4)—C(5)	1·335 (8)	C(5)—C(6)	1·396 (6)
C(6)—O(2)	1·370 (5)	O(1)—C(7)	1·401 (4)
O(2)—C(8)	1·361 (7)	C(9)—C(10)	1·393 (4)
C(9)—C(14)	1·412 (5)	C(10)—C(11)	1·393 (5)
C(10)—O(3)	1·355 (4)	C(11)—C(12)	1·370 (6)
C(12)—C(13)	1·367 (6)	C(13)—C(14)	1·397 (5)
C(14)—O(4)	1·355 (4)	O(3)—C(15)	1·377 (5)
O(4)—C(16)	1·416 (5)	C(17)—C(18)	1·394 (5)
C(17)—C(22)	1·395 (5)	C(18)—C(19)	1·392 (6)
C(18)—O(5)	1·351 (5)	C(19)—C(20)	1·351 (7)
C(20)—C(21)	1·368 (7)	C(21)—C(22)	1·397 (5)
C(22)—O(6)	1·372 (5)	O(5)—C(23)	1·408 (5)
O(6)—C(24)	1·394 (6)		
C(1)—P(1)—C(9)	99·2 (1)	C(1)—P(1)—C(17)	106·7 (1)
C(9)—P(1)—C(17)	107·3 (1)	P(1)—C(1)—C(2)	123·9 (2)
P(1)—C(1)—C(6)	120·2 (3)	C(2)—C(1)—C(6)	115·9 (3)
C(1)—C(2)—C(3)	122·2 (3)	C(1)—C(2)—O(1)	115·1 (3)
C(3)—C(2)—O(1)	122·7 (3)	C(2)—C(3)—C(4)	118·7 (4)
C(3)—C(4)—C(5)	121·7 (4)	C(4)—C(5)—C(6)	120·1 (4)
C(1)—C(6)—C(5)	121·2 (4)	C(1)—C(6)—O(2)	120·2 (3)
C(5)—C(6)—O(2)	118·4 (4)	C(2)—O(1)—C(7)	119·3 (3)
C(6)—O(2)—C(8)	116·1 (4)	P(1)—C(9)—C(10)	129·5 (2)
P(1)—C(9)—C(14)	113·5 (2)	C(10)—C(9)—C(14)	116·9 (3)
C(9)—C(10)—C(11)	121·1 (3)	C(9)—C(10)—O(3)	117·1 (3)
C(11)—C(10)—O(3)	121·8 (3)	C(10)—C(11)—C(12)	120·3 (4)
C(11)—C(12)—C(13)	121·0 (3)	C(12)—C(13)—C(14)	119·1 (4)
C(9)—C(14)—C(13)	121·7 (3)	C(9)—C(14)—O(4)	114·2 (3)
C(13)—C(14)—O(4)	124·1 (3)	C(10)—O(3)—C(15)	119·5 (3)
C(14)—O(4)—C(16)	119·1 (3)	P(1)—C(17)—C(18)	127·0 (3)
C(18)—C(17)—C(22)	117·0 (3)	P(1)—C(17)—C(22)	115·1 (3)
C(17)—C(18)—C(19)	120·6 (4)	C(17)—C(18)—O(5)	117·3 (3)
C(19)—C(18)—O(5)	122·0 (3)	C(18)—C(19)—C(20)	120·4 (4)
C(19)—C(20)—C(21)	121·5 (4)	C(20)—C(21)—C(22)	118·3 (4)
C(17)—C(22)—C(21)	122·1 (4)	C(17)—C(22)—O(6)	115·6 (3)
C(21)—C(22)—O(6)	122·4 (3)	C(18)—O(5)—C(23)	120·4 (3)
C(22)—O(6)—C(24)	118·6 (3)		

acetone solution. A Nicolet $R3m/V$ diffractometer (Cu $K\alpha$ radiation) was used to collect 3536 reflections, 3067 unique reflections ($R_{\rm int} = 0{\cdot}00\%$) of which 2528 were observed [$F > 6{\cdot}0\sigma(F)$]. Cell parameters were measured using 25 reflections $15 < 2\theta < 23°$, which were measured using Mo $K\alpha$ radiation and a crystal other than the one used to collect the full data set. Cell parameters determined from the crystal used to collect the full data set agreed with those reported here. 2θ was varied from 3·5 to 115·0°; $0 \le h \le 8$, $0 \le k \le 21$, $0 \le l \le 32$, two standard reflections being measured every 50 reflections with no significant change over the course of data collection.

Using the *SHELXTL-Plus* system of programs (Sheldrick, 1987) the structure was solved by direct methods and subjected to a full-matrix least-squares refinement on F, minimizing $w(F_o - F_c)^2$ with riding H atoms (fixed isotropic U), resulting in $R = 0{\cdot}0568$, $wR = 0{\cdot}0956$ [$w^{-1} = \sigma^2(F) + 0{\cdot}004069F^2$]. Largest $\Delta/\sigma = 0{\cdot}025$, $(\Delta\rho)_{\rm max} = 0{\cdot}32$, $(\Delta\rho)_{\rm min} = -0{\cdot}34$ e Å^{-3}. Extinction correction $\chi = 0{\cdot}0036$ (7) where $F^* = F[1 + 0{\cdot}002\chi F^2/\sin(2\theta)]^{-1/4}$. Atomic coordinates are given in Table 1.† Molecular geometry is summarized in Table 2.

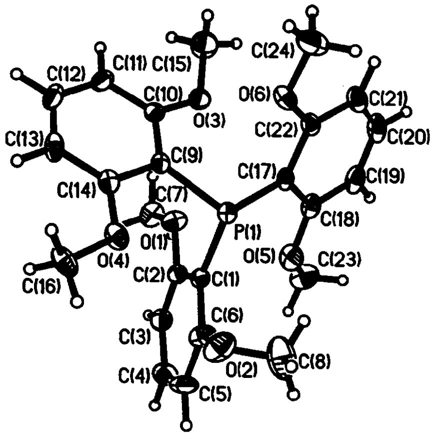

Fig. 1. *ORTEP* plot (Johnson, 1976) of (1), showing the numbering scheme. The phosphorus lone pair is perpendicular to the page, pointing toward the reader. 50% thermal ellipsoids are plotted for non-H atoms.

Discussion. Fig. 1 shows an *ORTEP* plot (Johnson, 1976) of (1). The average C—P bond length (1·844 Å) is only slightly longer than that of triphenylphosphine (2) (1·828 Å; Daly, 1964). Also the average C—P—C bond angle of (1) (104·4°) is quite similar to that of (2) (103·0°). Thus (1) appears to be essentially unhindered. This view may be confirmed

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53506 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

by comparison with a *bona fide* hindered triarylphosphine, *i.e.* tris(2,6-dimethylphenyl)phosphine, (3) (Sobolev, Chetkina, Romm & Gur'yanova, 1976). In this case, although the average C—P bond length (1·842 Å) is similar to that of (1), the average C—P—C bond angle (109·5°) is substantially enlarged.

In (1) the average P—C—C angle *syn* to the phosphorus lone pair [*e.g.* P(1)—C(1)—C(6)] is 116·3° and the average P—C—C angle *anti* to the phosphorus lone pair [*e.g.* P(1)—C(1)—C(2)] is 126·8°. While these are appreciably different from the idealized 120°, they are essentially the same as the corresponding averages in (2) (*i.e.* 116·1 and 124·0°) and (3) (*i.e.* 113·5 and 127·3°).

Phosphine (1) differs from (3) in one curious respect: the *ortho*-methyl groups of (3) are bent slightly *away* from the C—P bonds while the *ortho*-methoxy groups of (1) are bent slightly *toward* the C—P bonds. In (1) the average of all O—C—C angles analogous to O(6)—C(22)—C(17) is 116·6° while the average of O—C—C angles analogous to O(6)—C(22)—C(21) is 121·9°. For (3) the corresponding averages are 123·2 and 117·0°, respectively.

The angles that the planes of the aryl rings make with the plane defined by C(1), C(9) and C(17) are 95·2 [C(1)–C(6)], 43·7 [C(9)–C(14)] and 33·6° [C(17)–C(22)]. Thus two phenyls are tilted and one [C(1)–C(6)] is approximately parallel to the phosphorus lone pair. Five of the six methoxy groups lie approximately in the plane of the attached aromatic ring. Absolute values of the pertinent dihedral angles are: C(7)—O(1)—C(2)—C(3), 4·0; C(15)—O(3)—C(10)—C(11), 23·1; C(16)—O(4)—C(14)—C(13), 1·3; C(23)—O(5)—C(18)—C(19), 17·3; C(24)—O(6)—C(22)—C(21), 4·9°. One methoxy group lies approximately perpendicular to the plane of the attached aromatic ring, *e.g.* the dihedral angle C(8)—O(2)—C(6)—C(5) is 93·3°.

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Structural Studies of Systems with 'Very Short' Hydrogen Bonds. Structures of Methylammonium Hydrogen Succinate Monohydrate and Dimethylammonium Hydrogen Succinate at 110 K

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Abstract. Methylammonium hydrogen succinate monohydrate, $CH_6N^+.C_4H_5O_4^-.H_2O$, $M_r = 167{\cdot}16$, monoclinic, $P2_1/m$, $a = 4{\cdot}9788\ (5)$, $b = 13{\cdot}077\ (1)$, $c = 6{\cdot}133\ (2)$ Å, $\beta = 92{\cdot}34\ (1)°$, $V = 399{\cdot}0\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}391$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 1{\cdot}164$ cm^{-1}, $F(000) = 180$, $T = 110$ K, $R = 0{\cdot}035$ for 2627 observed reflections. Dimethylammonium hydrogen succinate, $C_2H_8N^+.C_4H_5O_4^-$, $M_r = 163{\cdot}17$, orthorhombic, $Cmcm$, $a = 6{\cdot}7863\ (9)$, $b = 8{\cdot}069\ (2)$, $c = 14{\cdot}284\ (3)$ Å, $V = 782{\cdot}2\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}386$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 1{\cdot}086$ cm^{-1}, $F(000) = 352$, $T = 110$ K, $R = 0{\cdot}028$ for 1142 observed reflections. In both compounds the hydrogen succinate ions are linked by 'very short' hydrogen bonds resulting in infinite chains. The O atoms involved in the short hydrogen bond are related by crystallographic symmetry in both salts, making the short hydrogen bond symmetric in a crystallographic sense. The H atom in the short hydrogen bond seems to be best described by two equally populated sites on each side of the centre of the hydrogen bond.

Introduction. Acid salts of carboxylic acids have earlier been thoroughly investigated by Speakman (1972). He classified these compounds in two groups.

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