3293 measured reflections
2220 independent reflections
1931 observed reflections
$[I > 2\sigma(I)]$

3 standard reflections
frequency: 90 min
intensity variation: none

Refinement

Refinement on F^2
Final $R(F) = 0.0401$ for $F > 4\sigma(F)$
$wR(F^2) = 0.1124$ for all data
$S = 1.058$
2217 reflections
220 parameters
Calculated weights
$w = 1/[\sigma^2(F_o^2)+(0.0496P)^2 + 0.3690P]$
where $P = (F_o^2+2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.000$
$\Delta\rho_{\max} = 0.177$ e Å^{-3}
$\Delta\rho_{\min} = -0.211$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (4)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.2055 (2)	0.7505 (2)	0.68972 (14)	0.0501 (4)
C2	0.2617 (2)	0.8493 (2)	0.6136 (2)	0.0474 (5)
C3	0.4263 (2)	0.8814 (2)	0.6367 (2)	0.0483 (5)
C4	0.4617 (2)	0.9575 (3)	0.7771 (2)	0.0536 (6)
C5	0.3705 (2)	0.8831 (3)	0.8588 (2)	0.0542 (6)
C6	0.2538 (2)	0.7932 (2)	0.8140 (2)	0.0475 (5)
C7	0.1587 (3)	0.7241 (2)	0.8965 (2)	0.0513 (6)
O7	0.2061 (2)	0.6433 (2)	0.9611 (2)	0.0793 (6)
O11	−0.1992 (2)	0.8743 (2)	0.8846 (2)	0.0762 (5)
C12	−0.0545 (3)	0.8757 (3)	0.8605 (2)	0.0518 (6)
O12	0.0040 (2)	0.9716 (2)	0.8188 (2)	0.0698 (5)
N13	0.0086 (2)	0.7527 (2)	0.8953 (2)	0.0473 (5)
C14	−0.0947 (3)	0.6830 (3)	0.9665 (2)	0.0602 (6)
C15	−0.2389 (3)	0.7444 (3)	0.9325 (3)	0.0811 (8)
O21	0.2290 (2)	0.7756 (2)	0.48796 (14)	0.0536 (4)
C22	0.0808 (3)	0.7943 (4)	0.4467 (3)	0.0892 (9)
C23	0.0438 (4)	0.6970 (5)	0.3220 (3)	0.1018 (11)
O31	0.5021 (2)	0.7388 (2)	0.6029 (2)	0.0577 (4)
C32	0.6369 (3)	0.7428 (3)	0.5531 (2)	0.0607 (6)
O33	0.6898 (2)	0.8546 (2)	0.5300 (2)	0.0875 (7)
C34	0.7080 (3)	0.5925 (3)	0.5339 (3)	0.0880 (10)
O41	0.4281 (2)	1.1152 (2)	0.8063 (2)	0.0636 (5)
C42	0.5407 (3)	1.2102 (3)	0.7716 (3)	0.0836 (9)
C43	0.4884 (5)	1.3693 (4)	0.8016 (4)	0.133 (2)

Table 4. *Selected geometric parameters* (Å, °) *for* (4)

O1—C6	1.361 (3)	C7—N13	1.384 (3)
O1—C2	1.452 (2)	O11—C12	1.338 (3)
C2—C3	1.506 (3)	O11—C15	1.440 (3)
C3—C4	1.525 (3)	C12—O12	1.192 (3)
C4—C5	1.492 (3)	C12—N13	1.391 (3)
C5—C6	1.316 (3)	N13—C14	1.455 (3)
C6—C7	1.492 (3)	C14—C15	1.499 (4)
C7—O7	1.210 (3)		
C6—O1—C2	113.7 (2)	N13—C7—C6	117.2 (2)
O1—C2—C3	111.5 (2)	C12—O11—C15	110.6 (2)
C2—C3—C4	110.5 (2)	O12—C12—O11	122.9 (2)
C5—C4—C3	110.0 (2)	O12—C12—N13	128.8 (2)
C6—C5—C4	122.6 (2)	O11—C12—N13	108.2 (2)
C5—C6—O1	125.5 (2)	C7—N13—C12	125.5 (2)
C5—C6—C7	122.7 (2)	C7—N13—C14	121.4 (2)
O1—C6—C7	111.8 (2)	C12—N13—C14	110.8 (2)
O7—C7—N13	119.6 (2)	N13—C14—C15	101.1 (2)
O7—C7—C6	123.2 (2)	O11—C15—C14	105.5 (2)

Both compounds were crystallized from diethyl ether at room temperature. Data were collected with a learnt profile method (Clegg, 1981). Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS*-90 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*-92 (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*-92.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71290 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1040]

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Structure of Methyltris(2,4,6-trimethoxyphenyl)phosphonium Iodide Ethanol Solvate

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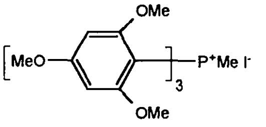
Abstract

The structure of methyltris(2,4,6-trimethoxyphenyl)phosphonium iodide, [CH_3TMPP]I, shows slightly-distorted tetrahedral geometry at phosphorus. There are no close anion–cation contacts.

Comment

We have been interested for some time in the use of phosphonium salts as materials for second-harmonic generation (SHG), and in their solid-state ^{31}P NMR spectra. There has been considerable interest in the use of the basic hindered phosphine, tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) as a ligand in organometallic chemistry (Chen & Dunbar, 1991), and the structure of $[CH_3TMPP]_2[Co_2Cl_6]$ has been determined (Dunbar, Quillevéré & Haefner, 1991). We considered it of interest to investigate the structure of a more mundane salt (I), as part of a series of alkyl–TMPP halides.



(I)

The salt was prepared by heating to reflux the phosphine and iodomethane in ethanol. It appears to contain poorly ordered ethanol of crystallization.

It is of interest to compare this structure with that of $[CH_3TMPP]_2[Co_2Cl_6]$. In the cation, bonds to phosphorus and angles about phosphorus are similar to those noted here. In the structures of TMPPSe and tris(2,6-dimethoxyphenyl)phosphine selenide (Allen, Bell, March & Nowell, 1990) there are said to be weak bonding interactions between phosphorus and the O atoms of *ortho*-methoxy groups with 'bonding' distances varying between 2.819 and 2.996 Å. These 'bonds' are attributed to an interaction between the lone pair at oxygen and a dipolar resonance form of the P=Se double bond. Such an interaction was also invoked in the description of the structure of $[Ph_2P(CH_2Ph)(C_6H_4\text{-}2\text{-}OMe)]Br$, in which the P—O distance is 2.88 Å (Wood, Wilkholm & McEwan, 1977). In our compound, these effects are equally pronounced; there are three shorter (2.820, 2.834, 2.779 Å) and three longer (3.104, 3.070, 3.079 Å) P···O non-bonded distances. These effects were also noted for TMPPO (Chaloner, Harrison & Hitchcock, 1993) and $[CH_3TMPP]_2[Co_2Cl_6]$.

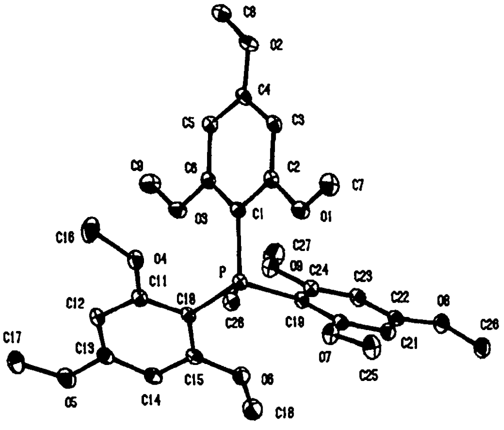


Fig. 1. Molecular structure and numbering scheme for the $(CH_3TMPP)^+$ cation.

Experimental

Crystal data

$C_{28}H_{36}O_9P^+.\ I^-.0.25C_2H_6O$
M_r = 686.0
Orthorhombic
Pbca
a = 13.155 (9) Å
b = 33.433 (5) Å
c = 14.634 (5) Å
V = 6436.4 $Å^3$
Z = 8
D_x = 1.41 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 14–15°
μ = 1.09 mm^{-1}
T = 298 K
Cube
0.4 × 0.4 × 0.25 mm
White
Crystal source: recrystallized from ethanol

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.54, T_{max} = 1.27
8545 measured reflections
8545 independent reflections
5045 observed reflections $[|F^2|>2\sigma|F^2|]$
θ_{max} = 25°
h = 0 → 17
k = 0 → 44
l = 0 → 18
2 standard reflections
frequency: 60 min
intensity variation: −2.2%

Refinement

Refinement on F
Final R = 0.059
wR = 0.081
S = 2.3
5045 reflections
361 parameters
H-atom parameters not refined
$w = \sigma^{-2}(F)$
$(\Delta/\sigma)_{max}$ = 0.6
$\Delta\rho_{max}$ = 1.32 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.14 e $Å^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
I	0.04112 (3)	0.12752 (1)	0.06464 (3)	0.0662 (1)
P	0.10465 (8)	0.11245 (3)	−0.45035 (7)	0.0304 (2)
O1	0.2336 (2)	0.1798 (1)	−0.4451 (2)	0.047 (2)
O2	0.1627 (2)	0.2322 (1)	−0.1521 (2)	0.045 (2)
O3	−0.0100 (2)	0.1147 (1)	−0.2650 (2)	0.043 (2)
O4	0.1496 (2)	0.0592 (1)	−0.3052 (2)	0.046 (2)
O5	−0.1362 (3)	−0.0299 (1)	−0.3393 (3)	0.059 (2)
O6	−0.0749 (2)	0.0735 (1)	−0.5506 (2)	0.047 (2)
O7	0.1857 (2)	0.1384 (1)	−0.6386 (2)	0.045 (2)
O8	−0.1057 (3)	0.2202 (1)	−0.7124 (2)	0.051 (2)
O9	−0.0896 (2)	0.1447 (1)	−0.4383 (2)	0.045 (2)

C1	0.1168 (3)	0.1461 (1)	−0.3538 (3)	0.032 (2)
C2	0.1847 (3)	0.1787 (1)	−0.3630 (3)	0.034 (2)
C3	0.1978 (3)	0.2065 (1)	−0.2958 (3)	0.037 (2)
C4	0.1432 (3)	0.2035 (1)	−0.2155 (3)	0.036 (2)
C5	0.0736 (3)	0.1722 (1)	−0.2024 (3)	0.036 (2)
C6	0.0596 (3)	0.1448 (1)	−0.2714 (3)	0.034 (2)
C7	0.3159 (4)	0.2066 (2)	−0.4573 (4)	0.058 (3)
C8	0.1032 (4)	0.2328 (2)	−0.0711 (3)	0.051 (3)
C9	−0.0751 (4)	0.1132 (2)	−0.1883 (4)	0.060 (3)
C10	0.0332 (3)	0.0680 (1)	−0.4224 (3)	0.032 (2)
C11	0.0638 (3)	0.0463 (1)	−0.3465 (3)	0.036 (2)
C12	0.0097 (4)	0.0130 (1)	−0.3151 (3)	0.042 (2)
C13	−0.0772 (3)	0.0018 (1)	−0.3633 (3)	0.043 (2)
C14	−0.1080 (3)	0.0220 (1)	−0.4418 (3)	0.041 (2)
C15	−0.0533 (3)	0.0542 (1)	−0.4722 (3)	0.036 (2)
C16	0.1727 (5)	0.0456 (2)	−0.2152 (4)	0.077 (3)
C17	−0.1076 (5)	−0.0532 (2)	−0.2627 (4)	0.074 (3)
C18	−0.1709 (4)	0.0672 (2)	−0.5934 (4)	0.063 (3)
C19	0.0468 (3)	0.1424 (1)	−0.5379 (3)	0.033 (2)
C20	0.0921 (3)	0.1535 (1)	−0.6207 (3)	0.034 (2)
C21	0.0418 (3)	0.1790 (1)	−0.6818 (3)	0.040 (2)
C22	−0.0523 (3)	0.1933 (1)	−0.6587 (3)	0.039 (2)
C23	−0.1011 (3)	0.1828 (1)	−0.5790 (3)	0.039 (2)
C24	−0.0510 (3)	0.1576 (1)	−0.5193 (3)	0.035 (2)
C25	0.2434 (4)	0.1544 (2)	−0.7121 (4)	0.058 (3)
C26	−0.0630 (4)	0.2309 (2)	−0.7987 (4)	0.057 (3)
C27	−0.1892 (4)	0.1562 (2)	−0.4123 (4)	0.063 (3)
C28	0.2273 (3)	0.0933 (1)	−0.4838 (3)	0.040 (2)
C29*	0.4495 (11)	0.4957 (5)	0.0073 (11)	0.106 (10)

* Occupancy 0.5, scattering factor equal to the average of O and C.

Table 2. *Selected intermolecular distances* (Å) *and angles* (°)

P—C1	1.813 (4)	P—C10	1.806 (4)
P—C19	1.797 (4)	P—C28	1.804 (4)
C1—P—C10	112.3 (2)	C1—P—C19	104.3 (2)
C1—P—C28	110.7 (2)	C10—P—C19	113.6 (2)
C10—P—C28	103.6 (2)	C19—P—C28	112.5 (2)

H atoms were fixed at idealized positions with $U_{\rm iso} = 1.3 \times U_{\rm eq}$ of the parent atom. $\sigma(F^2) = [\sigma^2(I) + (0.4I)^2]^{0.5}/{\rm Lp}$. Function minimized was $\Sigma w(|F_o|-|F_c|)^2$. Two peaks, C(29) and its equivalent lying across an inversion centre, were included as a molecule of ethanol, disordered and at half occupancy.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry, and a diagram of the unit-cell contents have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71292 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1047]

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Three Isomers of Tricyclo[10.3.0.0^{4,9}]pentadecane-2,10-dione, (I), (II) and (III), and *cis-cisoid-cis*-9-Hydroxy-9-methyltricyclo[9.3.0.0^{3,7}]tetradecan-2-one, (IV)

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Abstract

The crystal structures of the four title compounds, which were obtained during studies of the preparation and reactions of 6–8–5 and 5–8–5 fused-ring compounds, have been determined by X-ray diffraction. (I), (II) and (III) are *cis-cisoid-cis*, *trans-cisoid-cis* and *trans-transoid-cis* isomers of the 6–8–5 fused-ring compound, respectively. The eight-membered ring takes a boat–chair form in compounds (I) to (IV).

Comment

Syntheses of 5–8–5 fused-ring compounds and the conformations of their eight-membered rings have been investigated previously (Okumoto, Ohba, Saito, Umehara & Hishida, 1988; Umehara *et al.*, 1990). The syntheses of the 6–8–5 fused-ring compounds (I)–(III) (Umehara *et al.*, 1993) and methylation of