isotropically; for compound (2), H atoms were fixed in calculated positions with $U_{iso} = 1.3U_{eq}$ of the parent atom and not refined.

We thank the SERC and Zeneca for a SERC CASE award (to PGS).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: HU1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Berg, J.-E., Karlsson, B., Pilotti, A. M. & Söderholm, A. C. (1978). *Acta Cryst.* B**34**, 2041–2042.

Burden, R. S., Kemp, M. S., Wiltshire, C. W. & Owen, J. D. (1984). *J. Chem. Soc. Perkin Trans.* 1, pp. 1445–1448.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Fitzgerald, L. J., Gallucci, J. C., Gerkin, G. E. & Rawal, V. H. (1991). *Acta Cryst.* C**47**, 2134–2137.

Hazlet, S. E. & Dornfield, C. A. (1941). *J. Am. Chem. Soc.* **66**, 1781–1782.

Hubbard, C. R., Mighell, A. D. & Pomerantz, I. H. (1978). *Acta Cryst.* B**34**, 2381–2384.

Keumi, U., Umeda, T., Inoue, Y. & Kitajima, H. (1989). *Bull. Chem. Soc. Jpn*, **62**, 89–95.

Keumi, T., Yamada, H., Takahashi, H. & Kitajima, H. (1982). *Bull. Chem. Soc. Jpn*, **55**, 629–630.

Reppart, W. J., Gallucci, J. C., Lundstedt, A. P. & Gerkin, G. E. (1984). *Acta Cryst.* C**40**, 1572–1576.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Wägner, A. & Malmros, G. (1979). *Acta Cryst.* B**35**, 2220–2222.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1995). C**51**, 2683–2685

Hexyltris(2,4,6-trimethoxyphenyl)-phosphonium Iodide

PENNY A. CHALONER, R. M. HARRISON AND PETER B. HITCHCOCK

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton, England

(*Received* 18 *January* 1994; *accepted* 21 *November* 1994)

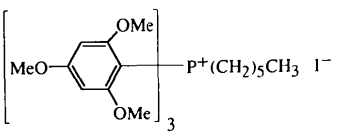
Abstract

The structure of hexyltris(2,4,6-trimethoxyphenyl)-phosphonium iodide, $[(C_6H_{13})(C_9H_{11}O_3)_3P]^+.I^-$, [HexylTMPP]I, shows slightly distorted tetrahedral geometry at the P atom. The alkyl chains are extended in parallel pairs.

©1995 International Union of Crystallography
Printed in Great Britain – all rights reserved

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 structures of $[CH_3TMPP][Co_2Cl_6]$ (Dunbar, Quillevéré & Haefner, 1991) and $[CH_3TMPP]I$ (Chaloner, Harrison & Hitchcock, 1993) have been determined.



[HexylTMPP]I

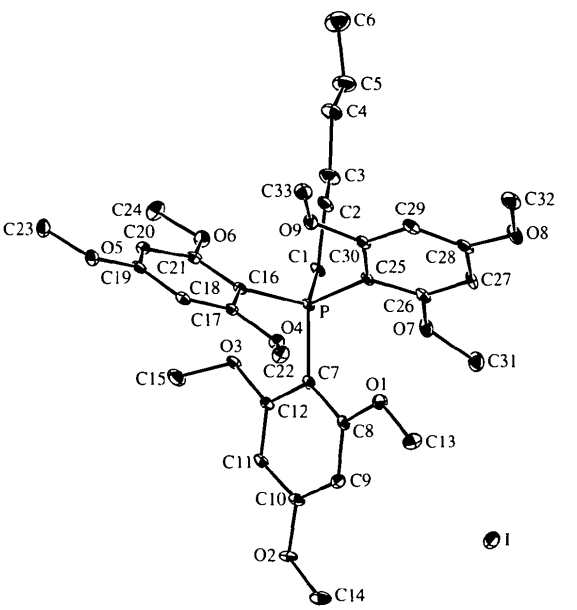


Fig. 1. Molecular structure and numbering scheme for [HexylTMPP]I.

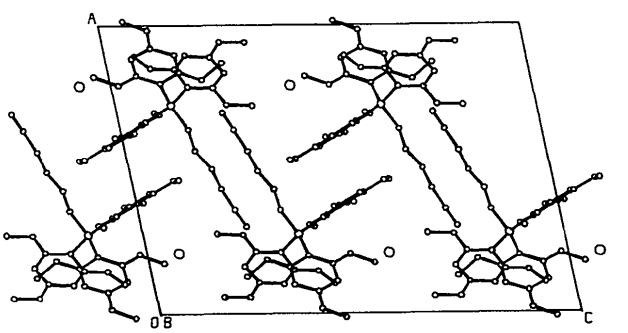


Fig. 2. Packing diagram for [HexylTMPP]I.

It is of interest to compare the structure of the title compound, [HexylTMPP]I, with those of other compounds containing $[CH_3TMPP]^+$. The geometries about the P atoms and of the aryl rings are similar with only minor deviations due to packing. The notable feature in the title compound is the alignment of the alkyl chains in head-to-tail-related molecules (Fig. 2).

Experimental

The salt was prepared by heating (323 K) the phosphine and 1-iodohexane in ethanol for 2 h. Good quality crystals were obtained by slow evaporation from aqueous ethanol solution. The solid material discoloured slowly (to yellow–brown) on exposure to air and light.

Crystal data

$C_{33}H_{46}O_9P^+.I^-$
M_r = 744.6
Monoclinic
$P2_1/c$
a = 15.922 (6) Å
b = 9.591 (4) Å
c = 23.019 (9) Å
β = 102.34 (3)°
V = 3434.0 Å^3
Z = 4
D_x = 1.44 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9–10°
μ = 1.02 mm^{-1}
T = 298 K
Needle
0.4 × 0.3 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
5302 measured reflections
5115 independent reflections

3984 observed reflections [$|F^2| > 2\sigma(F^2)$]
R_{int} = 0.02
θ_{max} = 23°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 10$
$l = -25 \rightarrow 25$
2 standard reflections frequency: 60 min intensity decay: 1.3%

Refinement

Refinement on F
R = 0.041
wR = 0.049
S = 1.6
3984 reflections
397 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 2.0 e Å^{-3} (near I)
$\Delta\rho_{min}$ = −0.3 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *MolEN* (Fair, 1990)

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

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

	x	y	z	U_{eq}
I	0.20942 (2)	0.12860 (3)	0.07440 (1)	0.037 (1)
P	0.27546 (6)	0.62467 (12)	−0.13149 (5)	0.018 (1)
O1	0.20637 (18)	0.55190 (31)	−0.01834 (12)	0.027 (1)
O2	0.01758 (17)	0.18821 (32)	−0.11333 (13)	0.028 (1)
O3	0.18779 (16)	0.44878 (31)	−0.21885 (12)	0.023 (1)
O4	0.14886 (17)	0.78660 (31)	−0.10274 (12)	0.024 (1)
O5	0.05810 (18)	1.05181 (33)	−0.27778 (13)	0.030 (1)
O6	0.27407 (18)	0.69424 (33)	−0.26360 (12)	0.029 (1)
O7	0.37155 (18)	0.48007 (31)	−0.03134 (13)	0.030 (1)
O8	0.46365 (21)	0.85453 (36)	0.09989 (14)	0.043 (2)
O9	0.30710 (9)	0.93583 (32)	−0.10018 (13)	0.031 (1)
C1	0.3590 (2)	0.5436 (5)	−0.1620 (2)	0.023 (2)
C2	0.4318 (3)	0.6433 (5)	−0.1674 (2)	0.030 (2)
C3	0.4969 (3)	0.5728 (6)	−0.1964 (2)	0.042 (3)
C4	0.5659 (3)	0.6697 (6)	−0.2085 (2)	0.048 (3)
C5	0.6399 (3)	0.5930 (6)	−0.2307 (3)	0.056 (3)
C6	0.6976 (4)	0.6888 (7)	−0.2498 (3)	0.068 (3)
C7	0.2010 (2)	0.4935 (4)	−0.1183 (2)	0.019 (2)
C8	0.1736 (2)	0.4681 (4)	−0.0650 (2)	0.020 (2)
C9	0.1133 (2)	0.3651 (4)	−0.0618 (2)	0.023 (2)
C10	0.0777 (2)	0.2908 (4)	−0.1124 (2)	0.023 (2)
C11	0.1010 (2)	0.3153 (5)	−0.1660 (2)	0.021 (2)
C12	0.1612 (2)	0.4159 (4)	−0.1683 (2)	0.019 (2)
C13	0.1761 (3)	0.5361 (5)	0.0351 (2)	0.036 (2)
C14	−0.0142 (3)	0.1652 (5)	−0.0609 (2)	0.036 (2)
C15	0.1295 (3)	0.4304 (7)	−0.2742 (2)	0.056 (3)
C16	0.2130 (2)	0.7467 (4)	−0.1820 (2)	0.020 (2)
C17	0.1523 (2)	0.8232 (4)	−0.1589 (2)	0.019 (2)
C18	0.1022 (3)	0.9252 (5)	−0.1907 (2)	0.023 (2)
C19	0.1095 (2)	0.9478 (5)	−0.2491 (2)	0.023 (2)
C20	0.1646 (3)	0.8712 (5)	−0.2750 (2)	0.023 (2)
C21	0.2170 (2)	0.7709 (4)	−0.2413 (2)	0.020 (2)
C22	0.1061 (3)	0.8752 (5)	−0.0691 (2)	0.033 (2)
C23	0.0589 (3)	1.0787 (5)	−0.3389 (2)	0.037 (2)
C24	0.2777 (3)	0.7094 (6)	−0.3248 (2)	0.039 (2)
C25	0.3332 (2)	0.7067 (5)	−0.0643 (2)	0.020 (2)
C26	0.3752 (3)	0.6190 (5)	−0.0184 (2)	0.027 (2)
C27	0.4180 (3)	0.6709 (5)	0.0360 (2)	0.032 (2)
C28	0.4207 (3)	0.8134 (5)	0.0451 (2)	0.031 (2)
C29	0.3833 (3)	0.9044 (5)	0.0002 (3)	0.030 (2)
C30	0.3412 (3)	0.8508 (5)	−0.0540 (2)	0.024 (2)
C31	0.3868 (3)	0.3833 (5)	0.0167 (2)	0.040 (2)
C32	0.4662 (3)	1.0012 (6)	0.1124 (2)	0.045 (3)
C33	0.3020 (3)	1.0821 (5)	−0.0894 (2)	0.036 (2)

Table 2. *Selected geometric parameters* (Å, °)

P—C1	1.807 (5)	P—C7	1.799 (4)
P—C16	1.793 (4)	P—C25	1.803 (4)
C1—P—C7	109.3 (2)	C1—P—C16	112.4 (2)
C1—P—C25	103.8 (2)	C7—P—C16	105.8 (2)
C7—P—C25	113.2 (2)	C16—P—C25	112.5 (2)

H atoms were fixed at calculated positions with $U = 1.3U_{eq}$ of the parent atom.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

We thank the SERC for a grant (to RMH).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Chaloner, P. A., Harrison, R. M. & Hitchcock, P. B. (1993). *Acta Cryst.* C**49**, 1852–1854.
Chen, S. J. & Dunbar, K. R. (1991). *Inorg. Chem.* **30**, 2018–2023.
Dunbar, K. R., Quillevéré, A. & Haefner, S. C. (1991). *Acta Cryst.* C**47**, 2319–2321.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1995). C**51**, 2685–2687

Photochemistry of Dimethyl 1,8-Dichloro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

STEVEN J. RETTIG, JOHN R. SCHEFFER, JAMES TROTTER AND JIE YANG

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

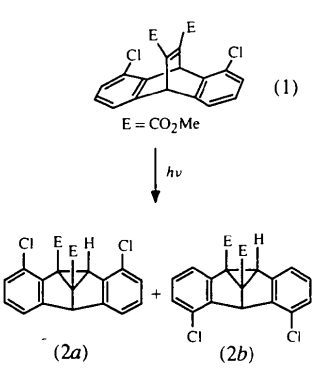
(*Received* 31 *March* 1995; *accepted* 16 *June* 1995)

Abstract

The molecule of the title compound, (1), $C_{20}H_{14}Cl_2O_4$, has geometry and dimensions similar to those of related materials; one ester group is fully conjugated with the C=C double bond and the other is non-conjugated. Photolysis of (1) produces two dibenzosemibullvalenes, the reaction being controlled mainly by intramolecular steric effects of the Cl substituents.

Comment

The 1,8-dichlorodibenzobarrelene diester (1) undergoes the di-π-methane reaction both in solution and in the solid state to give two regioisomeric dibenzosemibullvalenes, (2*a*) and (2*b*). The molecular structure of (1) was established by X-ray analysis and those of the photoproducts (2*a*) and (2*b*) from NMR data (Yang, 1993; Jones, Rettig, Scheffer, Trotter & Yang, 1995). The ratio (2*a*):(2*b*) is about 30:70 in solution and 10:90 in solid-state photolyses.



The molecular structure of (1) (Fig. 1 and Table 2) is similar to that of related materials (Jones *et al.*, 1995). The external angles at the ring junctions are enlarged as a result of steric strain, those adjacent to the Cl substituents being larger [mean 127.8 (2)°] than the remote angles [mean 125.9 (2)°]; the Cl—C—C(junction) angles are also slightly larger [mean 120.7 (1)°] than the Cl—C1—C2 type angles [mean 119.2 (1)°]. The two methoxycarbonyl groups exhibit different amounts of conjugation with the C11=C12 double bond. The group adjacent to the Cl substituents has a C=C—C=O dihedral angle of −177.3 (2)° (for the molecule of Table 1 and Fig. 1; the crystals are racemic), $\cos^2$(angle) = 1.00, and is thus fully conjugated. This conformation probably results from possible Cl···O steric repulsions if the group were rotated from the conjugated position. The remote ester group has a dihedral angle of −94.0 (2)°, $\cos^2$(angle) = 0.00, and is thus non-conjugated. The C—CO_2Me bond distances reflect these differences in conjugation, being 1.478 (2) Å for the conjugated group and 1.492 (2) Å for the non-conjugated group (Allen, 1981).

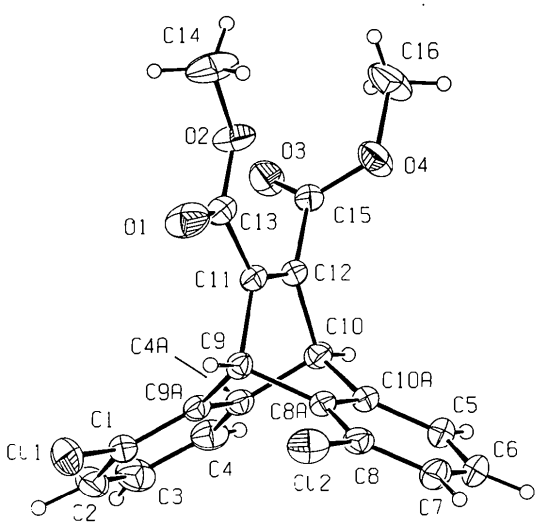


Fig. 1. View of the molecule with 33% probability displacement ellipsoids.

The major photoproduct (particularly in the solid state) is (2*b*); this is formed by initial vinyl–benzo bridging involving a benzo C atom *meta* to the Cl substituents [nearer the viewer in the above scheme; C12···C4a or C12···C10a in Fig. 1]. From considerations of the electronic effects of the Cl substituents, initial *ortho* bridging is predicted, as a result of greater electron density at the *ortho* C atom and of more extensive electron delocalization in the resulting biradical (Santiago, Houk, Snow & Paquette, 1976; Snow, Cottrell & Paquette, 1977; Jones *et al.*, 1995); thus, considering the electronic effects of the Cl substituents, (2*a*) is predicted to be the major photoproduct.

©1995 International Union of Crystallography
Printed in Great Britain – all rights reserved