organic compounds

Polymeric methylenebis(diphenyl-phosphine oxide) hydrogen triiodide

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The conformation of the cationic part of the title compound, $[\{(C_6H_5)_2POH_{0.5}\}_2CH_2]I_3$ or $dppmO_2H^+ \cdot I_3^-$ (dppm is diphenylphosphinomethane), is determined by hydrogen bonds between cations of monoprotonated $[(C_6H_5)_2P(=O)]_2CH_2$ (dppmO$_2$). Symmetric $P=O\cdots H\cdots O=P$ bridging, with H atoms lying on centres of inversion, leads to chain-like polymeric cations, $(dppmO_2H^+)_x$, made up of $H\cdots OP(C_6H_5)_2-CH_2-(C_6H_5)_2PO\cdots$ moieties. These are, in turn, cross-connected by non-classical $C-H\cdots I$ contacts between the $(dppmO_2H^+)_x$ methylene-group H atoms and the terminal I atoms of the triiodide anions, which display crystallographic inversion symmetry.

Comment

Extending our study of supramolecular structures of (iodoseleno)phosphonium salts (Seppälä *et al.*, 1999; du Mont *et al.*, 2001*a,b*) to bidentate ligands, we reacted $[(C_6H_5)_2P(=Se)]_2CH_2$ (dppmSe$_2$) with two equivalents of diiodine in dichloromethane (Boraei & du Mont, 2000). Attempted crystallization of the iodine adduct was accompanied by hydrolytic reactions, due to the presence of moist air, affording a small fraction of the new title compound, (I).

The salt-like compound (I) (Fig. 1) consists of helical polymeric cations, $(dppmO_2H^+)_x$, made up of $\cdots H\cdots OP(C_6H_5)_2-CH_2-(C_6H_5)_2PO\cdots$ moieties, and triiodide anions, which interconnect these chains through $C-H\cdots I-I-I$ interactions ($C-H\cdots I$ 2.89 and 2.83 Å) with the H atoms of the $(dppmO_2H^+)_x$ methylene groups. These rather short non-classical hydrogen-bond contacts are in the range of those observed in 2,5-bis[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-1,3,4,6-tetrathiapentalene triiodide ($C-H\cdots I$ 2.832 Å; Mori *et al.*, 1994) and in 1-azoniapropellane triiodide ($C-H\cdots I$ 2.897 Å; Bakshi *et al.*, 1996).

The $P=O$ bond-lengthening arising from coordination with bridging H^+ is, at *ca* 0.05 Å, less than in true hydroxy-phosphonium cations, R_3POH^+ (Ruthe *et al.*, 2000), but similar

to that in the bis-AlCl$_3$ complex $[dppmO_2(AlCl_3)_2]$ (Sangokoya *et al.*, 1989).

(I)
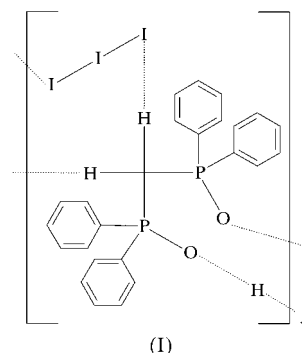
The $P=O\cdots H\cdots O=P$ bridges and $I-I-I$ groups in (I) are centrosymmetric, with the central H and I atoms lying on centres of inversion. The $P=O\cdots H\cdots O=P$ bonding within the polymeric cation, $(dppmO_2H^+)_x$, is closely related to that of known molecular centrosymmetric bis(phosphine oxide)-hydrogen(I) cations in $[(Me_3PO)_2H]^+ \cdot AuI_2^-$ (Godfrey *et al.*, 1996) and in $[(^iPr_3PO)_2H]^+ \cdot I_3^-$ (Ruthe *et al.*, 2000). As in the latter triiodide salt, $O\cdots O$ distances in (I) [mean 2.384 Å] are slightly shorter than in the comparable non-centrosymmetric compound $[TPO_3H]I_3$ [2.432 (10) Å], where H^+ is chelated by two $R_2R'P=O$ donor functions derived from the tridentate chelate ligand bis(*o*-diphenylphosphinophenyl)(phenyl)-phosphane (Bigoli *et al.*, 1992).
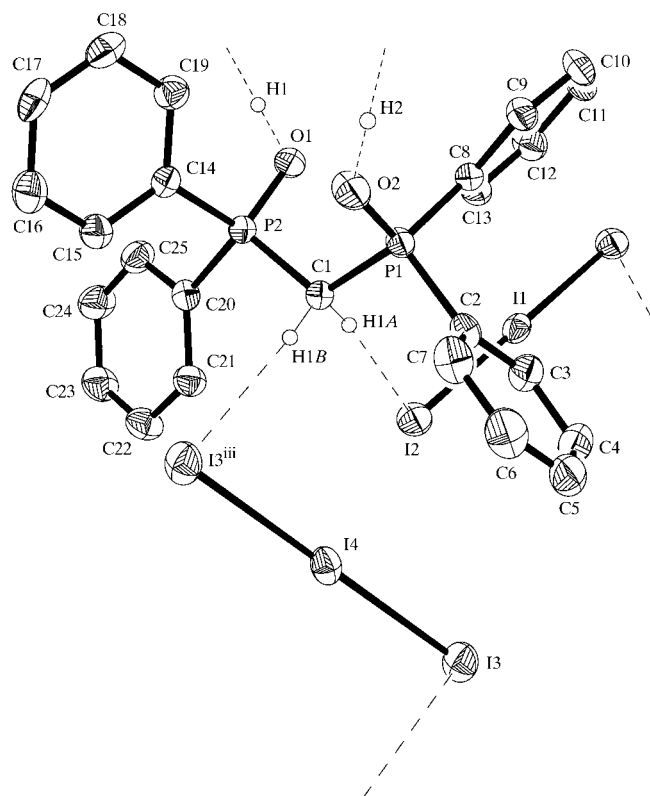

Figure 1
The structure of (I) with displacement ellipsoids drawn at the 50% probability level and arbitrary H-atom radii. H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonds are indicated by dashed lines [symmetry code: (iii) $1 - x$, $1 - y$, $1 - z$].
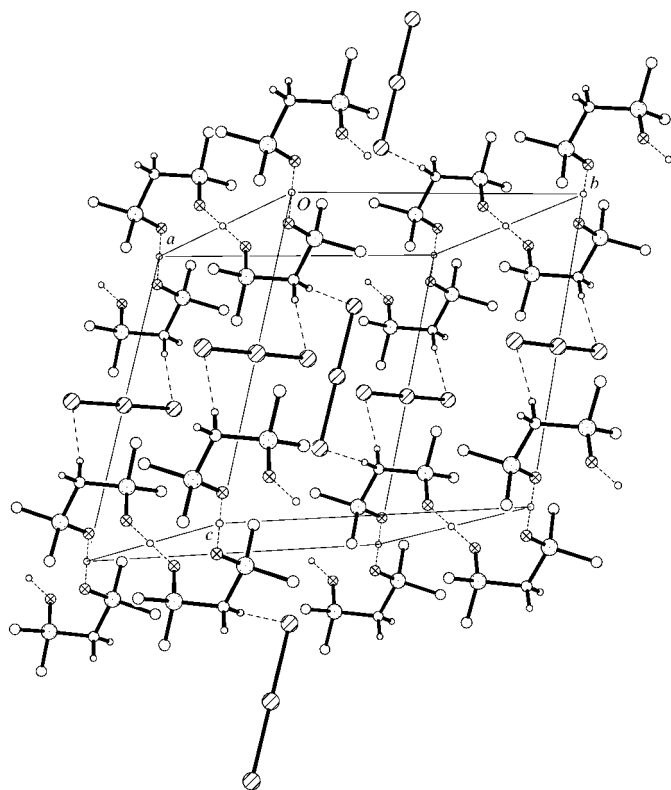
Figure 2
A packing diagram for (I). H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonds are indicated by dashed lines. Ring C atoms, except for *ipso*-C atoms, have been omitted.

The packing of solid (I) can be described as corrugated layers of helical $(dppmO_2H^+)_x$ cations, whose methylene groups are centres of further bifurcating hydrogen-bond systems $(-H\cdots I-I-I\cdots H-C-H\cdots I-I-I\cdots H-)$ cross-linking these cationic layers, leading to a complex three-dimensional network (Fig. 2). The conformation of the helical $(dppmO_2H^+)_x$ cations is apparently determined by the geometric requirements of, first, linear $O\cdots H\cdots O$ bridges [different from the chelate $(dppmO_2)_3Na^+$; Hewertson *et al.* (1979)], secondly, wide P—O—H angles, and thirdly, preferred torsion angles, such as those of the ligands dppm [by considering the P electron lone pairs as pseudo-ligands (Schmidbaur *et al.*, 1988)], $dppmO_2$ (Antipin *et al.*, 1980), $dppmS_2$ (Carmalt *et al.*, 1996) and $dppmSe_2$ (Carroll & Titus, 1977; Ahrens & Jones, 1997).

Experimental

A dichloromethane solution of $dppmSe_2$ and diiodine in a 1:2 molar ratio was stirred at room temperature for 3 h. Orange single crystals of (I) were obtained after exposing a small portion of the reaction mixture in an NMR tube to moist air for one week at room temperature with slow evaporation of the solvent. The formulation of the product was satisfactorily established by ^{31}P NMR spectra and by mass spectrometry (FAB, *o*-nitrobenzylamine matrix). ^{31}P NMR (δ, p.p.m., CH_2Cl_2/C_6D_6 solution): 42.6; mass spectrometry: m/z (%) = 417 {30, $[Ph_2P(O)CH_2P(OH)Ph_2]^+$}, appeared when a partially hydrolysed sample from $dppmSe_2I_4$ (Boraei & du Mont, 2000) was studied by FAB-MS.

Crystal data

$C_{25}H_{22}O_2P_2\cdot H^+\cdot I_3^-$	$Z = 2$
$M_r = 798.07$	$D_x = 1.914$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.1284$ (8) Å	Cell parameters from 10 022
$b = 11.8155$ (10) Å	reflections
$c = 12.5299$ (10) Å	$\theta = 3$–$30°$
$\alpha = 110.852$ (2)°	$\mu = 3.52$ mm^{-1}
$\beta = 93.855$ (2)°	$T = 143$ (2) K
$\gamma = 96.043$ (2)°	Rectangular prism, orange
$V = 1384.61$ (19) Å^3	$0.37 \times 0.20 \times 0.15$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer	8330 independent reflections
	6921 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.033$
Absorption correction: multi-scan	$\theta_{max} = 30.6°$
(*SADABS*; Bruker, 1998)	$h = -14 \rightarrow 14$
$T_{min} = 0.384$, $T_{max} = 0.590$	$k = -16 \rightarrow 16$
16 933 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 0.832P]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
8330 reflections	$\Delta\rho_{max} = 2.65$ e Å^{-3}
294 parameters	$\Delta\rho_{min} = -1.07$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

I1—I2	2.9066 (3)	P1—C1	1.801 (3)
I3—I4	2.9052 (3)	P2—O1	1.521 (2)
P1—O2	1.518 (2)	P2—C14	1.786 (3)
P1—C2	1.785 (3)	P2—C1	1.789 (3)
P1—C8	1.797 (3)	P2—C20	1.789 (3)
O2—P1—C2	111.33 (15)	C14—P2—C1	112.64 (13)
O2—P1—C8	113.60 (14)	O1—P2—C20	112.58 (14)
C2—P1—C8	108.01 (13)	C14—P2—C20	107.07 (13)
O2—P1—C1	106.93 (13)	C1—P2—C20	106.98 (13)
C2—P1—C1	105.14 (13)	P2—O1—H1	123.93 (17)
C8—P1—C1	111.53 (13)	P1—O2—H2	133.03 (19)
O1—P2—C14	110.52 (13)	P2—C1—P1	117.57 (15)
O1—P2—C1	107.08 (13)		
O1—P2—C1—P1	53.25 (19)	O2—P1—C1—P2	57.3 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O2^i	1.19	1.19	2.380 (4)	180
O1—H1$\cdots$O1^{ii}	1.19	1.19	2.388 (4)	180
C1—H1$A\cdots$I2	0.99	2.83	3.818 (3)	173
C1—H1$B\cdots$I3^{iii}	0.99	2.89	3.878 (3)	176

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $-x, -y, -z$; (iii) $1 - x, 1 - y, 1 - z$.

All H atoms, except H1 and H2, were refined using a riding model starting from calculated positions, with $U_{iso}(H) = 1.2U_{eq}(C)$, and effective C—H distances of 0.99 Å for methylene H and 0.95 Å for aromatic H atoms. Atoms H1 and H2 were found and refined satisfactorily on special positions (inversion centres) with no indication of

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disorder, although X-ray methods alone cannot determine the H-atom positions with absolute certainty. The maximum residual electron density was 0.94 Å from atom I3.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1492). Services for accessing these data are described at the back of the journal.

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