

Hydrogen bis[tris(4-fluorophenyl)-phosphane oxide] triiodide

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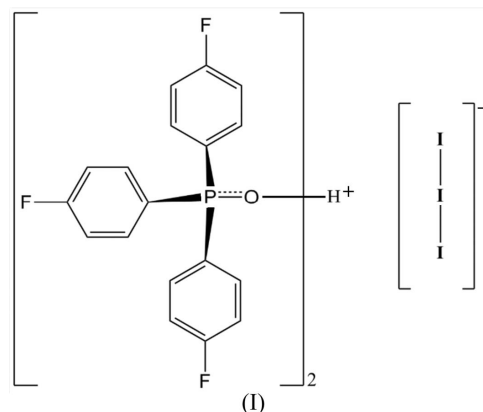
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In the title compound, $C_{36}H_{25}F_6O_2P_2 \cdot I_3^-$, hydrogen-bonded $[(p\text{-FC}_6\text{H}_4)_3\text{PO}]_2\text{H}^+$ dimers assemble along the crystallographic c axis to form channels that house extended chains of triiodide anions. Although the $I-I$ bond lengths of 2.9452 (14) and 2.9023 (15) Å are typical, the inter-ion $I \cdots I$ distance of 3.5774 (10) Å is unusually short. *A posteriori* modelling of nonmerohedral twinning about (100) has been only partially successful, achieving a reduction in the maximum residual electron density from 5.28 to 3.24 $e \text{ \AA}^{-3}$. The inclusion of two low-occupancy I-atom sites (total 1.7%), which can be interpreted as translational disorder of the triiodide anions along the channels, reduced the maximum residual electron density to 2.03 $e \text{ \AA}^{-3}$. The minor fractional contribution volume of the nonmerohedral twin domains refined to 0.24 and simultaneous refinement of the inversion twin domains showed the crystal to be a 0.5:0.5 inversion twin.

Comment

The title structure, (I), consists of triiodide anions and H^+ counter-ions that link pairs of tris(4-fluorophenyl)phosphane oxide entities into hydrogen-bonded dimers (Fig. 1). The two crystallographically unique $(p\text{-FC}_6\text{H}_4)_3\text{PO}$ molecules have similar conformations, as indicated by their $O-P-C-C$ torsion angles of 3.9 (11), 78.0 (12) and -13.7 (13)° involving $O1-P1$, and of 80.2 (12), 10.1 (13) and -15.5 (12)° involving $O2-P2$ (Table 1). This type of parallel-parallel-orthogonal conformation has been named 'orthogonal flipper' by Dance & Scudder (2000) and is also the conformation adopted in an analogous unfluorinated structure with FeBr_4^- as the counter-ion (corresponding torsion angles = 19.5, 27.3 and 83.2, and 19.5, 27.3 and 83.2°; Lane *et al.*, 1994). However, when the counter-ion is ClO_4^- , a rotor-type conformation is adopted (corresponding torsion angles = 29.9, 37.3 and 64.1, and 16.2, 30.0 and 42.7°; Antipin *et al.*, 1980). In the structure of (I), the orthogonal rings are opposite each other in the hydrogen-bonded dimers and participate in face-to-face π interactions. In contrast, each orthogonal ring is opposite a parallel one in

the unfluorinated dimer reported by Lane *et al.* (1994), facilitating edge-to-face π interactions.



In the structure of (I), the $P-O$ bonds of 1.526 (10) and 1.530 (10) Å are significantly longer than typical double $P=O$ bonds of, for example, 1.487 (3) Å in $(C_6H_5)_3P=O$ (Thomas & Hamor, 1993) and 1.467 (2) Å in $(C_6F_5)_3P=O$ (Nicholson & Thwaite, 2003). However, they are shorter than the single $P-O$ bonds of 1.581 (4), 1.579 (4) and 1.553 (3) Å in triphenylphosphane oxyl derivatives (Kunnari *et al.*, 2001; Carcedo *et al.*, 2004; Chow *et al.*, 1996), which average 1.571 Å. As the $P-O$ bond lengths fall midway between single- and double-bond values, it is clear that the correct depiction of these bonds should be as intermediate single/double bonds. Because of this, and as the H atom was not found in the

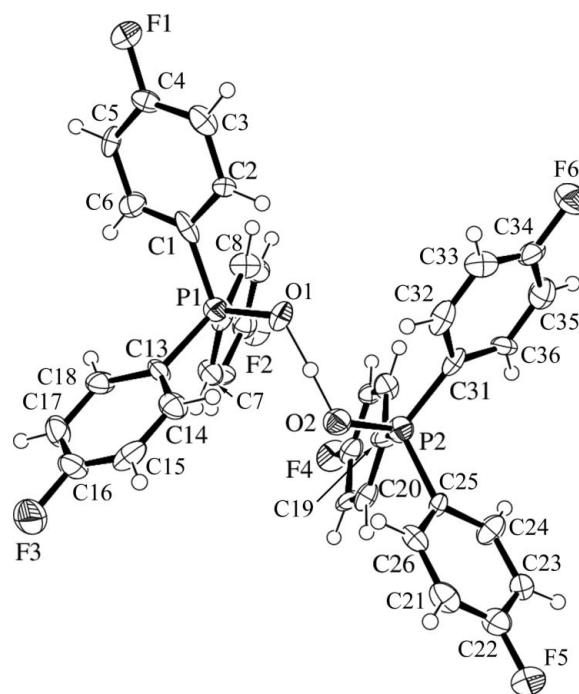


Figure 1

A view of the $[(p\text{-FC}_6\text{H}_4)_3\text{PO}]_2\text{H}^+$ dimer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

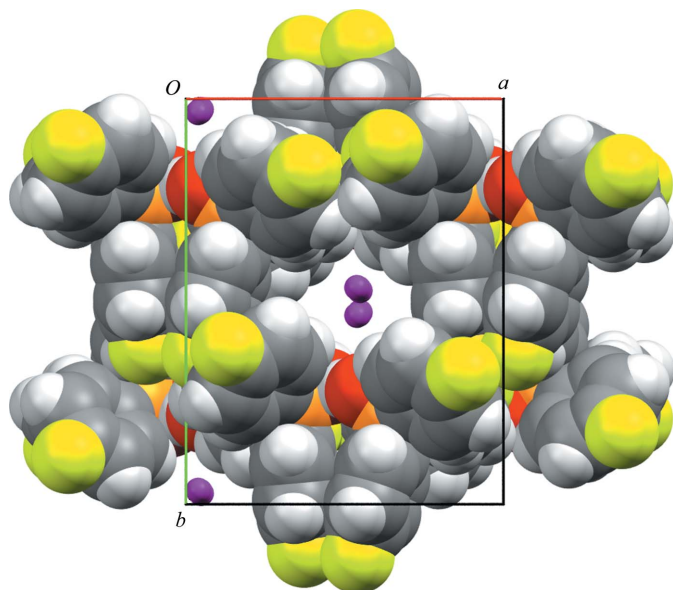


Figure 2
A packing diagram for (I), viewed down the *c* axis, showing the channels that house the triiodide anions.

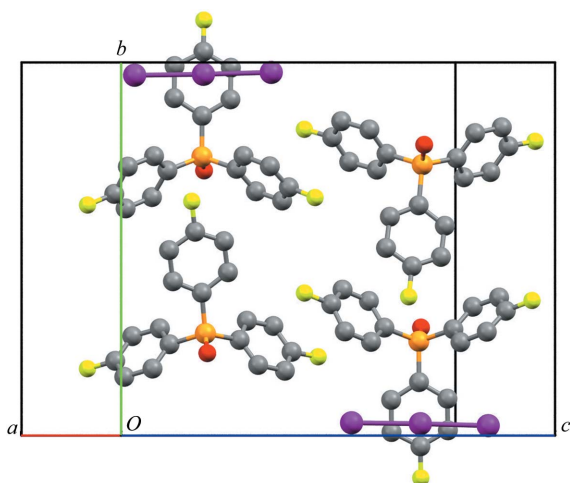


Figure 3
A view of the packing of (I) in the vicinity of the *bc* plane, showing local noncrystallographic twofold and mirror symmetries, which act as a twinning plane.

difference electron-density map, it has been fixed at the initial halfway position between the O atoms in this strong hydrogen bond (Table 2), with its displacement parameter refined freely. Although this is reasonable it may not be strictly correct, as asymmetric positioning of the H atom is common in even the strongest hydrogen bonds; see, for example, Konu & Chivers (2006) and Antipin *et al.* (1980), who found that the $O \cdots H \cdots O$ bond in $[(C_6H_5)_3P=O]_2H^+ \cdot ClO_4^-$ changes from symmetric at room temperature to asymmetric on cooling.

Packing of the hydrogen-bonded dimers of (I) forms tunnels parallel to the crystallographic *c* axis (Fig. 2). The tunnels house triiodide anions, which are also aligned along the crystallographic *c* axis. Within each tunnel, adjacent iodide anions are related by crystallographic *c*-glide operations. In stacked structures or structures with channels, triiodides often

form infinite linear chains with weak $I_3^- \cdots I_3^-$ interactions, with typical $I \cdots I$ separations ≥ 3.6 Å (Svensson & Kloo, 2003). The $I \cdots I$ distance of 3.5774 (11) Å seen in (I) is a rare example of an interionic $I_3^- \cdots I_3^-$ separation of less than 3.6 Å. In contrast, the most significant contact between the triiodide anion and the surrounding tunnel atoms is 3.156 Å between phenyl atom H32 and the central iodine atom I1, which is only marginally shorter than the van der Waals contact (3.35 Å; Harrison, 1978).

The two I—I bonds [2.9023 (15) and 2.9452 (14) Å] show significant asymmetry. This is not unusual and is caused by nonbonded interactions within the crystal structure. In the case of (I), the most significant sub-van der Waals contacts involving the terminal triiodide I atoms are $I \cdots I$ contacts, which are of equal length for symmetry reasons. However, atom I2 has five $I \cdots H$ contacts shorter than the sum of the van der Waals radii (3.283–3.347 Å), compared with only two for I3 (3.222 and 3.291 Å).

Experimental

For the preparation of the title compound, (*p*-FC₆H₄)₃P (0.418 g, 1.32 mmol) was dissolved in anhydrous diethyl ether (30 ml). To this was added iodine (two equivalents, 0.671 g, 2.64 mmol), which caused rapid precipitation of a brown solid. The reaction was stirred for 48 h, after which time the solid was isolated by standard Schlenk techniques. Crystals were prepared by dissolving the brown solid in dichloromethane (5 ml) in a Rotaflo tube. Hexane (15 ml) was layered on top of the solution and the layers were allowed to diffuse slowly over a period of 48 h, after which time purple–brown crystals of (I) had formed.

Crystal data

$C_{36}H_{25}F_6O_2P_2^+ \cdot I_3^-$	$V = 3710.8$ (2) Å ³
$M_r = 1046$	$Z = 4$
Monoclinic, <i>Cc</i>	Mo $K\alpha$ radiation
$a = 13.2153$ (4) Å	$\mu = 2.68$ mm ⁻¹
$b = 15.9752$ (6) Å	$T = 100$ K
$c = 18.5695$ (6) Å	$0.18 \times 0.15 \times 0.06$ mm
$\beta = 108.818$ (2)°	

Data collection

Nonius KappaCCD area-detector diffractometer	14255 measured reflections
Absorption correction: multi-scan (<i>SORTAV</i> ; Blessing, 1995)	5376 independent reflections
$T_{\min} = 0.645$, $T_{\max} = 0.856$	4363 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.081$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.131$	$\Delta\rho_{\max} = 2.03$ e Å ⁻³
$S = 1.05$	$\Delta\rho_{\min} = -1.60$ e Å ⁻³
5376 reflections	Absolute structure: Flack (1983),
466 parameters	with 1024 Friedel pairs
17 restraints	Flack parameter: 0.50 (3)

C-bound H atoms were idealized with C–H bond lengths of 0.95 Å and with the H atom on the external bisector of the C–C–C angle, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Initial refinement with anisotropic displacement parameters for all non-H atoms converged to $R_1 = 0.0659$, with a maximum $\Delta\rho_{\max}$ of 5.79 e Å⁻³.

Table 1

Selected geometric parameters (Å, °).

C1–P1	1.811 (15)	O1–P1	1.526 (10)
C7–P1	1.783 (13)	O2–P2	1.530 (10)
C13–P1	1.799 (12)	I1–I3	2.9023 (15)
C19–P2	1.740 (15)	I1–I2	2.9452 (14)
C25–P2	1.799 (14)	I2–I3 ⁱ	3.5774 (11)
C31–P2	1.797 (14)		
O1–P1–C7	112.9 (6)	O2–P2–C19	112.4 (6)
O1–P1–C13	109.4 (6)	O2–P2–C31	110.5 (5)
O1–P1–C1	107.4 (6)	O2–P2–C25	107.0 (6)
C8–C7–P1–O1	78.0 (12)	C20–C19–P2–O2	80.2 (12)
C14–C13–P1–O1	–13.7 (13)	C32–C31–P2–O2	–15.5 (12)
C2–C1–P1–O1	3.9 (11)	C26–C25–P2–O2	10.1 (13)

Symmetry code: (i) $x, -y + 1, z + \frac{1}{2}$

A posteriori screening for twinning by looking for $F_o^2 \gg F_c^2$ was carried out using *PLATON* (Spek, 2009). A nonmerohedral twin, with {100} as the twin plane (Fig. 3) and with twin matrix (1 0 0.459, 0 –1 0, 0 0 –1), was identified and used to construct expanded reflection files, in which overlapping reflections were assigned indices for each contributing twin domain. The inclusion of inversion twins gave a total of four domains: (i) the initial domain, (1 0 0, 0 1 0, 0 0 1); (ii) the inverse of (i), (–1 0 0, 0 –1 0, 0 0 –1); (iii) a nonmerohedral twin, (1 0 0.459, 0 –1 0, 0 0 –1); and (iv) the inverse of (iii), (–1 0 –0.459, 0 1 0, 0 0 1).

Three expanded reflection files were generated using three different 2θ resolution tolerance criteria for establishing nonmerohedral reflection overlap, namely 0.05, 0.10 and 0.15°, which gave 465, 863 and 1210 overlapping reflections, respectively. Refinements carried out using these reflection files, in which the fractional contribution volumes of the above domains were allowed to vary, were compared on the basis of *R* factors, bond-length s.u. values, mean (F_o^2)/mean (F_c^2) distribution versus $F_c/F_c(\text{max})$ and $\Delta\rho_{\text{max}}$, and, in each case, the 0.05° data were found to be the best, e.g. $\Delta\rho_{\text{max}}$ values for the 0.05, 0.10 and 0.15° 2θ tolerance data were 3.24, 4.02 and 5.28 e Å^{–3}, respectively. All further structure refinement was therefore carried out using the 0.05° data. The fractional contribution volumes refined to 0.37 (3), 0.38 (3), 0.124 (6) and 0.123 (6) for domains (i)–(iv), respectively. The last two numbers were restrained to be equal because of the high correlation between the two parameters (–0.99).

Ideally, twinning should be dealt with at the data-processing stage, but this was not possible with the version of the diffractometer software being used in the current case. Given the rudimentary method used to assign nonmerohedral reflection overlap, i.e. a global 2θ tolerance parameter, which assumes average reflection width, shape and twin obliquity, it is reasonable to anticipate that further improvements could be achieved if the software examined each reflection on a more individual basis, allowing for crystal anisotropy and the way the area detector intersects the Ewald sphere. Also, the small changes that are automatically made to the orientation matrix to compensate for slight crystal movement during the data collection could also be taken into account, rather than assuming a fixed orientation matrix.

In fact, the nonmerohedral twin correction was only partially successful and left rows of residual electron-density peaks spanning the cell in the *z* direction near the triiodide ions, with an inter-peak separation of approximately half an I–I bond, which also approximates to *c*/12. The two highest remaining peaks in the residual

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H12P···O2	1.203	1.228	2.431 (13)	179

electron-density map were suitably positioned to be modelled as a translational disorder of the triiodide anions along the channels. They were therefore treated as disordered minor I-atom sites I2*B* and I3*B*, whose occupancies refined to 0.021 (4) and 0.030 (4), respectively, reducing $\Delta\rho_{\text{max}}$ to 2.03 e Å^{–3}. The minor-site displacement parameters were subjected to ‘rigid-body’ restraints, in which the anisotropic displacement parameters in the direction of their I–I bonds, I2–I3*B* and I3–I2*B*, were restrained to be equal. Also, the U^{ij} values for the minor I-atom sites were restrained to be equal to those of the major I-atom sites they are bonded to, as the I atoms in the minor sites are generated from those in the major sites by translation of the triiodide along the channels parallel to *c*.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *DIRDIF08* (Beurskens *et al.*, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3082). Services for accessing these data are described at the back of the journal.

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