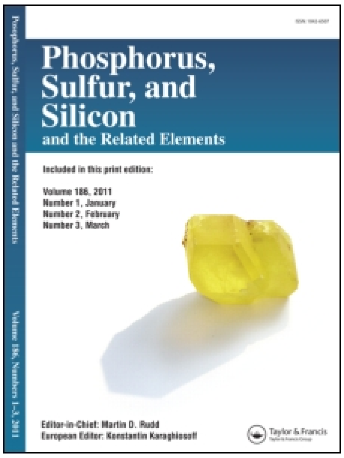

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REACTION OF DIIODINE WITH BIS-(O-DIPHENYLPHOSPHINOPHENYL) PHENYLPHOSPHINE (TP). FORMATION, CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPOUND [TPO$_3$H]I$_3$-C$_6$H$_5$CH$_3$

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REACTION OF DIIODINE WITH BIS-(O-DIPHENYLPHOSPHINOPHENYL) PHENYLPHOSPHINE (TP). FORMATION, CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPOUND [TPO_3H]I_3-$C_6H_5CH_3$

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A toluene solution of the title compound (TP) and an excess of diiodine gave, surprisingly, by slow evaporation of the solvent in the air, the product [TPO_3H]I_3-$C_6H_5CH_3$, where one of the three phosphinic P atoms of the TP, is oxidized to POH and two to P═O moieties, giving rise to a monocation [TPO_3H]$^+$. The X-ray structure of the compound has shown that the crystals are triclinic with $P\bar{1}$ space group, $a = 11.218(5)$, $b = 14.469(6)$, $c = 14.626(6)$ Å, $\alpha = 93.67(2)$, $\beta = 94.50(2)$, $\gamma = 91.88(2)°$, $V = 2360(2)$ Å^3, $Z = 2$. Solution and refinement of intensity data gave final residuals of $R = 0.0512$. The cation shows a conformation with a ten membered ring depending on the intramolecular hydrogen bond between the two extreme oxygen atoms and on O---H(C_{ph}) interactions. The bond lengths P(1)—O(1), P(2)—O(2), P(3)—O(3) follow the order: 1.510(8), 1.486(7), 1.504(8) Å respectively, as expected by the existence of the hydrogen bond between H(1) and O(3). The O—P—C_{phenyl} bond angles fall in the 107.1(5)–114.3(5)° range. The triiodide anion is nearly linear [I(1)—I(2)—I(3) 178.2(1)°] and shows moderately asymmetric bond lengths [I(1)—I(2) 2.871(2) I(2)—I(3) 2.969(3) Å].

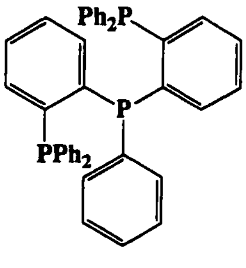
Key words: Diiodine; poly-arylphosphines; poly-arylphosphine-oxides; X-ray; triiodides.

INTRODUCTION

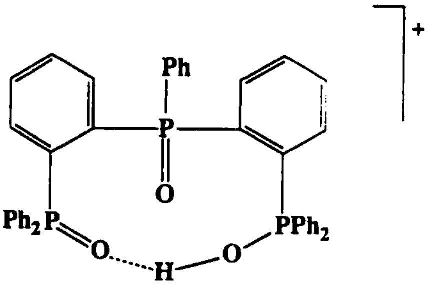
The interaction of I_2 with *n*-donors can give rise to charge-transfer complexes which may either be inert compounds or intermediates in redox reactions.[1] We are interested in this topic, and until now the reactions involving thioamido donors[2,4] have been investigated. As an extension we have decided to investigate the behaviour of other *n*-donors, as phosphines. As a preliminary result, we report in this paper the unexpected reaction product obtained by reacting bis-(*o*-diphenylphosphinophenyl)phenylphosphine (TP)[5], with I_2, according to the following reaction scheme:

$$TP + 9I_2 + 3H_2O \rightarrow 5H^+ + TPO_3H^+ + 6I_3^-$$

The molecules TP and TPO_3H^+ are drawn below, for reasons of clarity.



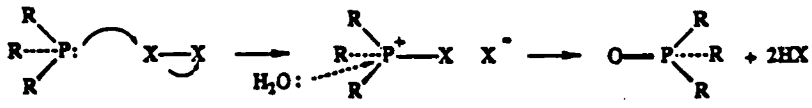
TP



TPO_3H^+

RESULTS AND DISCUSSION

The reaction of TP with I_2 in toluene, without protection against moisture, produces the new compound $[TPO_3H]^+I_3^-$, where two phosphorus atoms of the tritertiary phosphine are oxidized to P=O and one atom to P—OH, giving a monocation having as counter ion an I_3^-. It has been known for a long time that tertiary phosphines react with halogens to form R_3PX_2 derivatives,[6] but only recently structural[7] and solid state ^{31}P NMR spectroscopic[8] results have shown unambiguously that the products have ionic phosphonium salt structures $Ph_3PX^+X_n^-$ $(n = 1,3)$. Previous solution studies have led to rather confusing results. Rao *et al.*[9] reported to have observed the transformation of the outer charge-transfer complex Ph_3PI_2 in the inner complex $Ph_3PI^+I^-$; however experimental absorbances given to support the formation of the inner complex do not seem consistent with it, but rather with $Ph_3P{=}O$. Conductometric titrations of Ph_3P—I_2 system[10], under rigorously anhydrous conditions indicate the formation of the di- and tetra-halide. It is also reported that traces of water affect the reaction and the formation of $[Ph_3PH]^+I^-$ has been claimed.[11] On the other side, it is known that triphenylphosphine is resistant to air oxidation,[12] while by reacting Ph_3P with dihalogens in wet solvents the product is $Ph_3P{=}O$.[13] It is presumed that water attacks the initially formed halophosphonium cation according to the following reaction scheme:



We suggest that the isolated $[TPO_3H]^+$ is formed by attack of the water present in the solvent by a similar mechanism, and that the existence of the cation containing one hydroxylic group is probably related to the intramolecular hydrogen bond between the oxygen atoms (see later) which stabilizes the cation.

Structural Results

Fractional atomic coordinates are given in Table I; selected bond distances and angles are listed in Table II.

TABLE I

Fractional atomic co-ordinates (x10^4) with estimated standard deviations in parentheses

	X/a	Y/b	Z/c		X/a	Y/b	Z/c
I(1)	7230(1)	3446(1)	5503(1)	C(25)	2786(9)	3291(7)	5143(7)
I(2)	6224(1)	2763(1)	7086(1)	C(26)	2405(10)	2861(7)	5905(8)
I(3)	5106(1)	2054(1)	8690(1)	C(27)	2739(10)	3259(7)	6808(8)
P(1)	63(3)	1573(2)	2800(2)	C(28)	3451(10)	4065(7)	6907(8)
P(2)	2377(3)	2816(2)	4001(2)	C(29)	3816(10)	4488(7)	6162(8)
P(3)	1510(3)	1767(2)	5846(2)	C(30)	3499(10)	4094(7)	5285(7)
O(1)	-15(7)	997(5)	3620(5)	C(31)	961(10)	1678(7)	6950(7)
O(2)	2335(8)	1787(5)	3965(5)	C(32)	1611(11)	1319(8)	7665(8)
O(3)	446(7)	1740(5)	5151(5)	C(33)	1155(13)	1275(9)	8524(10)
C(1)	1317(11)	1344(8)	2153(8)	C(34)	62(15)	1578(10)	8666(11)
C(2)	1698(13)	1986(9)	1562(9)	C(35)	-626(16)	1923(11)	7941(11)
C(3)	2627(17)	1814(13)	997(12)	C(36)	-174(13)	1987(10)	7101(10)
C(4)	3133(18)	974(13)	1105(13)	C(37)	2468(10)	813(7)	5691(7)
C(5)	2852(17)	344(13)	1663(12)	C(38)	1996(12)	23(8)	5165(8)
C(6)	1882(14)	509(10)	2248(10)	C(39)	2685(13)	-752(10)	5087(10)
C(7)	-1232(10)	1272(7)	2033(7)	C(40)	3798(13)	-724(10)	5466(9)
C(8)	-1255(13)	1365(9)	1105(9)	C(41)	4296(14)	46(10)	5992(10)
C(9)	-2311(15)	1187(10)	536(11)	C(42)	3610(11)	829(8)	6094(8)
C(10)	-3316(13)	875(9)	921(10)	H(1)	122(91)	1362(68)	4360(85)
C(11)	-3299(12)	743(8)	1852(9)	C(43a)	749	4958	8969
C(12)	-2254(11)	947(8)	2415(8)	C(44a)	1463	4189	9010
C(13)	28(10)	2793(7)	3138(7)	C(45a)	2638	4288	9403
C(14)	955(9)	3292(7)	3655(7)	C(46a)	3099	5157	9754
C(15)	753(11)	4202(8)	3967(8)	C(47a)	2384	5927	9713
C(16)	-294(13)	4643(10)	3747(9)	C(48a)	1209	5828	9320
C(17)	-1199(14)	4141(10)	3221(10)	C(49a)	-517	4753	8452
C(18)	-1033(11)	3224(8)	2896(8)	C(43b)	1020	5385	9109
C(19)	3424(10)	3270(7)	3266(8)	C(44b)	1134	4438	8906
C(20)	3239(12)	4038(8)	2781(8)	C(45b)	2192	4016	9180
C(21)	4045(13)	4299(10)	2135(10)	C(46b)	3135	4541	9657
C(22)	4989(15)	3783(11)	2025(11)	C(47b)	3020	5487	9861
C(23)	5195(16)	3036(12)	2461(11)	C(48b)	1963	5909	9587
C(24)	4410(15)	2774(11)	3109(10)	C(49b)	-160	5613	8829

The conformation of the cation (Figure 1) depends on the intramolecular hydrogen bond between the two extreme oxygen atoms and on O---H(C_{ph}) interactions. In fact the hydroxylic hydrogen atom lies approximately between the two oxygen atoms [O(1)—H(1) 1.17(12), O(3)—H(1) 1.27(12) Å] giving rise to a ten membered ring through a very strong hydrogen bond [O(1)---O(3) 2.432(10) Å, O(1)—H(1)---O(3) 171(10)°]. The two Ph_2PO and the PhPO moieties assume a conformation in such a way that each oxygen lies approximately in the plane of each phenyl ring [range of the torsion angle values of the carbon atom eclipsing the oxygen atom: 19(1) 30(1)°]. The resulting C—H---O interactions [range of the contact values: 2.95(1) 3.11(2) Å for C---O and 2.53(1) 2.73(2) Å for H---O] are weak and do not influence the P—O distances (the P(2)—O(2) distance is 1.486(8) Å against 1.493(2) Å reported for Ph_3PO).[14] Also in the case of Ph_3PO adducts

TABLE II

Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

I(1)-I(2)	2.871(2)	P(2)-C(14)	1.81(1)
I(2)-I(3)	2.969(3)	P(2)-C(19)	1.79(1)
P(1)-O(1)	1.510(8)	P(2)-C(25)	1.78(1)
P(2)-O(2)	1.486(8)	P(3)-C(26)	1.84(1)
P(3)-O(3)	1.504(8)	P(3)-C(31)	1.78(1)
P(1)-C(1)	1.78(1)	P(3)-C(37)	1.79(1)
P(1)-C(7)	1.79(1)	O(1)-H(1)	1.17(12)
P(1)-C(13)	1.80(1)		
I(1)-I(2)-I(3)	178.2(1)	C(14)-P(2)-C(19)	105.9(5)
O(1)-P(1)-C(1)	114.3(5)	C(14)-P(2)-C(25)	106.3(5)
O(1)-P(1)-C(7)	107.1(5)	C(19)-P(2)-C(25)	107.9(5)
O(1)-P(1)-C(13)	110.9(5)	O(3)-P(3)-C(26)	113.3(5)
C(1)-P(1)-C(7)	105.8(5)	O(3)-P(3)-C(31)	107.6(5)
C(1)-P(1)-C(13)	110.5(5)	O(3)-P(3)-C(37)	113.6(5)
C(7)-P(1)-C(13)	107.9(5)	C(26)-P(3)-C(31)	106.5(5)
O(2)-P(2)-C(14)	113.1(5)	C(26)-P(3)-C(37)	109.4(5)
O(2)-P(2)-C(19)	112.5(5)	C(31)-P(3)-C(37)	106.0(5)
O(2)-P(2)-C(25)	110.8(5)	P(1)-O(1)-H(1)	119(5)

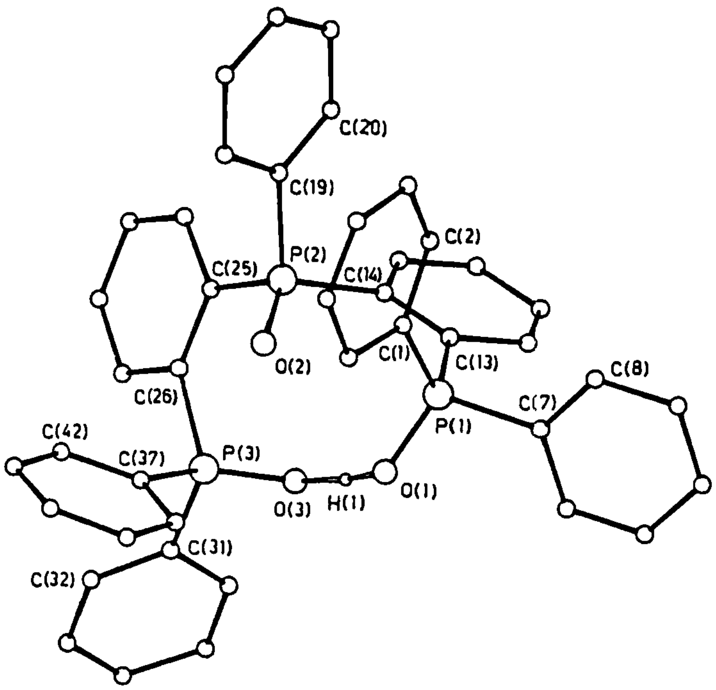


FIGURE 1 Perspective view of the cation.

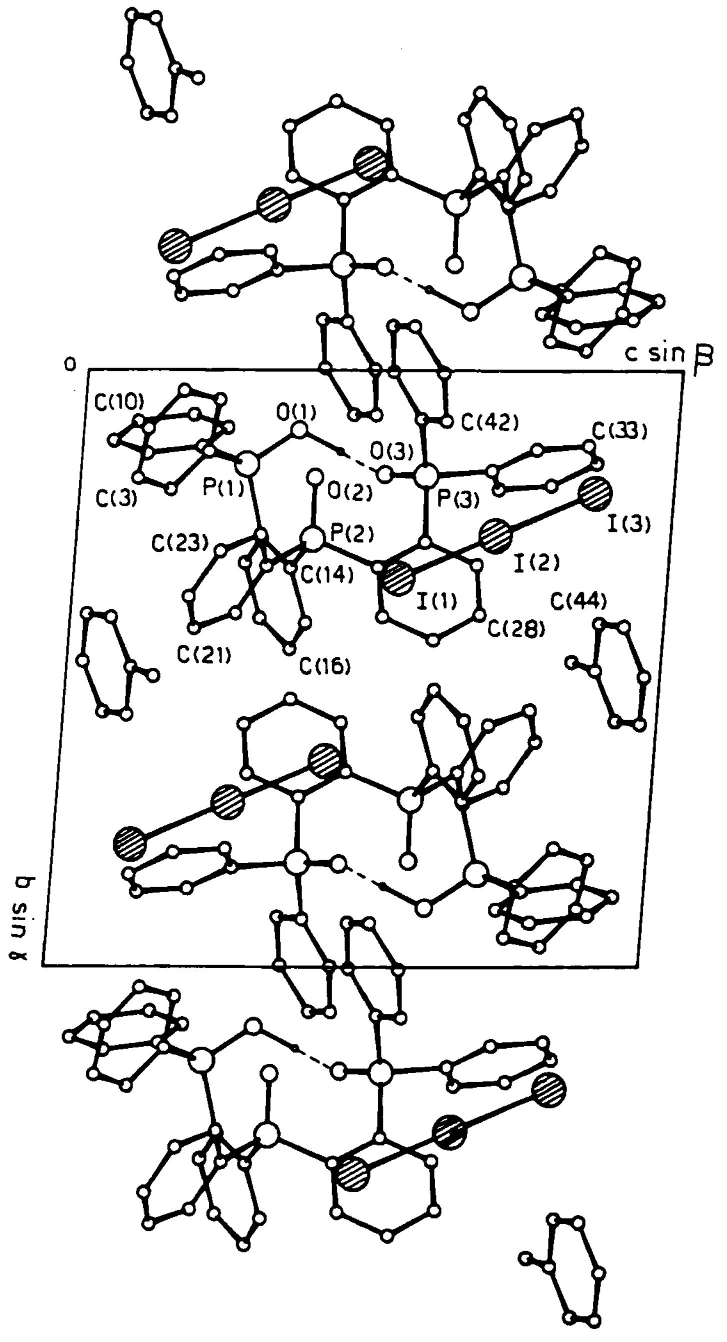


FIGURE 2 Projection of the structure along [100].

with molecules containing the H—X group (X = N, O, F)[14] where, even though hydrogen bonds of type PO---H—X exist, no significant lengthening of the P—O distances is observed. In the case of Ph_3PO---HCl, instead, the P—O distance is appreciably longer (1.517(2) Å).[14] In the molecule reported here, the hydrogen

TABLE III

Experimental data for the crystallographic analyses

formula	$C_{49}H_{42}I_3O_3P_3$
M	1152.504
crystal system	triclinic
space group	$P\bar{1}$
a/Å	11.218(5)
b/Å	14.469(6)
c/Å	14.626(6)
α/deg	93.67(2)
β/deg	94.50(2)
γ/deg	91.88(2)
V/Å^3	2360(2)
Z	2
Dc/Mg m^{-3}	1.622
F(000)	1128
temperature/K	295
crystal size/mm	0.11x0.25x0.47
diffractometer	CAD4
μ(Mo Kα)/cm^{-1}	21.03
scan type	$\theta/2\theta$
scan speed/deg min^{-1}	$\leqslant$ 3.3
scan width/deg	0.80+0.35 tgθ
radiation	Nb-filtered MoKα ($\bar{\lambda}$ = 0.71073 Å)
θ-range	3-26
reflections for lattice parameters number	25
θ-range	13-17
std reflcn measured after every 50	4 6 4 -1 5 8
h range	-13 13
k range	-17 17
l range	0 18
no. of meas.refl.	8301
condition for obs.	$I > 2\sigma(I)$
no. reflections used in the refinement	2889
no.refined parameters	251
R^a (Rw^a)	0.0512 (0.0703)
k,g ($w = K/\left[\sigma^2(F_o) + gF_o^2\right]$)	0.2314 0.008827
min/max height in final ΔF(eÅ^{-3})	-0.89/1.00

(a) $R = \sum|\Delta F|/\sum|F_o|$; $Rw = \left[\sum w(\Delta F)^2/\sum wF_o^2\right]^{1/2}$

bond produces a similar lengthening (P(1)—O(1) and P(3)—O(3) 1.510(8) and 1.504(8) Å, respectively). The triiodide anion is nearly linear [I(1)—I(2)—I(3) 178.2(1)°] and has a moderately asymmetric bond length distribution [I(1)—I(2)

I(2)—I(3) 2.970(3) Å] which is not determined by a specific set of interactions, the I(3) atom being not involved in interactions with other atoms.

The packing (Figure 2) is determined by van der Waals interactions between the cations and the anions, and the resulting channels running along [100] are occupied by the toluene guest.

EXPERIMENTAL

The ligand TP has been prepared according to literature data.[5] Well formed lustrous orange-brown crystals of $[TPO_3H]I_3 \cdot C_6H_5CH_3$ suitable for X-ray analysis have been obtained by slow evaporation in air of a toluene solution of TP and an excess of iodine. Toluene was Carlo Erba RPE-ACS reagent, and it has been used without further purification. Analytical results were in agreement with the above formulation. I.r. Spectra (cm^{-1}) were recorded on a Perkin Elmer mod 983 Spectrophotometer as KBr pellets: 3050w 1587w 1480w 1433m 1203m 1120s (P═O) 1000w 745s 725m 700m 541s 494w 355w.

Structure determination

All diffraction measurements were made on an Enraf-Nonius CAD4 automatic diffractometer, using graphite monochromatized Mo—kα radiation ($\lambda = 0.71073$ Å). The setting angles of 25 intense reflections ($13 < \Theta < 17°$) were used to determine accurate cell constants and orientation matrix, by least-squares fit. The data collections were performed by the ω—2Θ scan, within the limits $3° < \Theta < 26°$. A scan speed $\leq 3.3°$/min and a variable scan range of $(\alpha + 0.35 \tan \Theta)°$, with $\alpha = 0.80$ were used. The space group was to be $P\bar{1}$. Of 8301 independent reflections measured, 2889 were considered as observed $[I > 2\sigma(I)]$. The intensities were corrected for Lorentz and polarization effects, for absorption (maximum and minimum values 1.5219, 0.7732 respectively) and secondary extinction (maximum and minimum values 1.0203, 0.7838) following the empirical method of Walker and Stuart.[15] The structure was solved by the Patterson and Fourier technique and refined by block-matrix least squares, with anisotropic thermal parameters for I, P and O atoms using the SHELX 76[16] program. Only the hydroxylic hydrogen was located from a ΔF map; the coordinates of the hydrogen atoms of the phenyl groups placed at their geometrically calculated positions were not refined, but introduced in the final structure factor calculation with fixed isotropic thermal parameters ($U = 0.1303$ Å^2). The solvent molecule was found to be disordered and the corresponding non-hydrogen atoms were inserted in two position with 0.50 site occupancy factor, as found from the refinement; while the corresponding hydrogen atoms were not considered. Convergence was reached at R = 0.0512.

Experimental data for the crystallographic analyses are reported in Table III

Note. The tables of experimental data for the crystallographic analysis, of bond distances and angles, of coordinates for the hydrogen atoms, and of anisotropic or isotropic thermal parameters were deposited with the Cambridge Crystallographic Data Center (CCDC) U.K.

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