# Crystal and molecular structure of $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$

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The title compound crystallizes in the centrosymmetric triclinic space group  $P\overline{1}$  with Z = 4. The crystallographic asymmetric unit contains two independent cations; interatomic distances within these include P=O = 1.47(1) and 1.47(1)Å,  $P-C_6H_5 = 1.78(2)-1.81(1)$ Å and  $P-CH_2CH_2NMe_3^+ = 1.80(1)$  and 1.81(1)Å. The phosphine oxide moiety is involved in intermolecular hydrogen bonding  $(O\cdots H-C, \text{ with } O\cdots H \ge 2.42$ Å) and the iodide is involved in  $I\cdots H-C$  contacts with  $I\cdots H \ge 3.10$ Å.

**KEY WORDS:** Phosphine oxide; quaternary ammonium; water-soluble phosphine; crystal structure; hydrogen bonding.

# Introduction

Metal-carbonyl complexes of the water-soluble cationic phosphine derivative (2-diphenylphosphinoethyl)trimethylammonium iodide ("amphos iodide"),  $[(C_6H_5)_2P(CH_2CH_2N(CH_3)_3)^+][I^-]$ , were first reported some fifteen years ago.<sup>1</sup> Amphos iodide is of considerable interest as a ligand, since it has the potential to produce water-soluble analogs of those catalytically active transition-metal phosphine complexes which are normally soluble only in organic solvents. Such complexes have already been shown to be of utility as a catalysts in the hydrogenation, hydroformylation and telomerization of water-soluble organic substrates in aqueous solution.<sup>2,3</sup>

The title compound, a phosphine oxide derivative, was obtained as the penultimate product in the synthetic route to "amphos iodide" via the sequence shown in Scheme 1.<sup>4</sup> (It should be noted that the oxide func-

$$\begin{array}{c} (C_{6}H_{5})_{2}PCl \\ \downarrow +Li, -LiCl \\ (C_{6}H_{5})_{2}PLi \\ \downarrow +(CH_{3})_{2}N(CH_{2}CH_{2}Cl), -LiCl \\ (C_{6}H_{5})_{2}P(CH_{2}CH_{2}N(CH_{3})_{2}) \\ \downarrow \\ H_{2}O_{2}, -H_{2}O \\ (C_{6}H_{5})_{2}P(=O)(CH_{2}CH_{2}N(CH_{3})_{2}) \\ \downarrow +CH_{3}I \\ [(C_{6}H_{5})_{2}P(=O)(CH_{2}CH_{2}N(CH_{3})_{3})^{+}][I^{-}] \\ \downarrow +HSiCl_{3}, -HOSiCl_{3} \\ [(C_{6}H_{5})_{2}P(CH_{2}CH_{2}N(CH_{3})_{3})^{+}][I^{-}] \\ Scheme 1 \end{array}$$

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tion on phosphorus is a protecting group and allows the selective quaternization of the nitrogen atom by methyl iodide.) This phosphine oxide has now been characterized by a single-crystal X-ray diffraction study.

#### Experimental

# Preparation of $(C_6H_5)_2P(CH_2CH_2N(CH_3)_2)$

This was based upon an earlier reported synthesis, and involves the lithiation of  $(C_6H_5)_2PCl$ , followed by reaction with  $(CH_3)_2N(CH_2CH_2Cl)$ .<sup>3</sup>

# Preparation of $(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_2)$

 $(C_6H_5)_2P(CH_2CH_2N(CH_3)_2)$  (5.0 g, 0.020 mol) was dissolved in 15 mL deaerated acetone in a Schlenk flask purged with N<sub>2</sub>(g). A solution of 30% H<sub>2</sub>O<sub>2</sub> (2.25 ml, 0.020 mol) was added dropwise from a pressure equalizing addition funnel. The solution was refluxed for 1 hr. The mixture was cooled to room temperature. Solvent was removed *in vacuo* to reveal a white, pasty solid. Yields varied from 71 to 90%. <sup>1</sup>H NMR (CDCl)<sub>3</sub>): 7.65 (m, 4H, o-phenyl), 7.40 (m, 6H, p,mphenyl), 2.57 (m, 2H, PCH<sub>2</sub>), 2.42 (m, 2H, CH<sub>2</sub>N), 2.15 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P NMR (CDCl)<sub>3</sub>: 32.7 (s).

# Preparation of $(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$

 $(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_2)$  (7.5 g, 0.028 mol) was dissolved in 40 mL acetone in a Schlenk flask. Pure CH<sub>3</sub>I (20 g(8.8 mL), 0.14 mol) was collected from crude CH<sub>3</sub>I passed through a column of activated alumina (neutral) and added to the phosphine oxide solution. The entire flask was covered with aluminum foil. The mixture stirred for 4 hr. The resultant white solid was filtered through a medium frit and washed twice with 10 mL acetone. The solid was dried in vacuo. Yields obtained were 90 to 95%. Recrystallization was carried out by dissolving the compound in a minimum of boiling CH<sub>3</sub>CN and allowing it to slowly cool to room temperature. Yields after recrystallization were 38 to 42%. <sup>1</sup>H NMR (D<sub>2</sub>O): 7.4–7.8 (m's, 10H, phenyl), 3.52 (m, 2H, PCH<sub>2</sub>), 3.10 (s+m, 11H,  $N(CH_3)_3 + CH_2N$ ). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 7.83 (m, 4H, o-phenyl), 7.55 (m, 6H, p,m-phenyl), 3.50 (m, 2H,

PCH<sub>2</sub>), 3.11 (s+m, 11H, N(CH<sub>3</sub>)<sub>3</sub> + CH<sub>2</sub>N). <sup>31</sup>P NMR (D<sub>2</sub>O): 38.1 (s). <sup>31</sup>P NMR (d<sub>6</sub>-DMSO): 29.2 (s).

# The crystallographic study

A pale yellow crystal of  $[(C_6H_5)_2P(=O)]$  $(CH_2CH_2N(CH_3)_3)^+$  [I<sup>-</sup>], of approximate orthogonal dimensions  $0.4 \times 0.3 \times 0.2$  mm, was inserted and sealed into a 0.3-mm-diameter thin-walled glass capillary and was centered on a Siemens R3m/V automated four-circle diffractometer. Diffraction data were collected with graphite-monochromatized Mo  $K\overline{\alpha}$  ( $\overline{\lambda}$  = 0.710730Å) radiation. Unit cell dimensions and the crystal's orientation matrix were determined by a leastsquares analysis of the automatically centered setting angles (20,  $\omega$  and  $\chi$ , with  $\phi$  held constant) of 50 reflections, well dispersed in reciprocal space and having 2 $\theta$  values in the range 25–30°. The experimental technique used for data collection has been described at length previously.<sup>6</sup> Details specific to the present structural analysis are collected in Table 1. The following items should be noted.

1. The complex crystallizes in the triclinic system. Possible space groups are the noncentrosymmetric space group P1 or the centrosymmetric space group  $P\overline{1}$ . The latter was chosen on the basis of intensity statistics and frequency of occurrence data.<sup>7</sup> The correctness of this choice was confirmed by the successful solution of the structure in this higher symmetry space group.

2. The structure was solved by a combination of direct methods and difference-Fourier syntheses under the SHELXTL PLUS system of crystallographic routines<sup>8,9</sup> on a VAX station 3100 computer. Calculations were based upon the analytical form of the scattering factors for neutral atoms;<sup>10a</sup> corrections were made for both real and imaginary components of anomalous dispersion.<sup>10b</sup>

3. Hydrogen atoms were included in the appropriate idealized trigonal or (staggered) tetrahedral geometry based upon  $d(C-H) = 0.96 \text{\AA}^{11}$  and  $U = 0.08 \text{\AA}^{2}$ .

4. Refinement of positional and anisotropic displacement coefficients for all non-hydrogen atoms converged [ $\Delta/\sigma < 0.001$  for all parameters] with R =3.93% for those 1924 reflections with  $|F_0| > 6\sigma(F_0)$ and with R = 8.22% for all 3352 independent reflections. Final atomic coordinates are collected in Table 2.

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Crystal data	
Empirical formula	C <sub>17</sub> H <sub>23</sub> INOP
Color; habit	Pale yellow crystal
Crystal size (mm)	.4 × .3 × .2
Crystal system	Triclinic
Space group	PĪ
Unit cell dimensions	a = 11.414(4) Å
	b = 11.949(2) Å
	c = 14.208(6)  Å
	$\alpha = 77.79(3)^{\circ}$
	$\beta = 71.84(3)^{\circ}$
	$\gamma = 89.85(2)^{\circ}$
Volume	1795.4(10) Å <sup>3</sup>
Z	4
Formula weight	415.2
Density(calc.)	1.536 mg/m <sup>3</sup>
Absorption coefficient	1.850 mm <sup>-1</sup>
F(000)	832
Data collection	
Diffractometer used	Siemens B3m/V
Radiation	$M_0 K_{\alpha} (\lambda) = 0.71073 \text{ Å}$
Temperature (K)	205
Monochromator	Highly oriented graphite crystal
2A range	8 0 to 40 0°
Scan type	2 <del>0_0</del>
Scan speed	Constant: 2 00°/min in (a)
Scan range (w)	$0.95^{\circ}$ plus Ka-separation
Background measurement	Stationary crystal and stationary
2	counter at beginning and end of
	scan, each for 25.0% of total
	scan time
Standard reflections	3 measured every 97 reflections
Index ranges	$-11 \le h \le 0, -11 \le k \le 11$
	$-13 \leq \ell \leq 12$
Reflections collected	3380
Independent reflections	$3352 (R_{int} = 2.20\%)$
Reflections $> 6\sigma$	1924
Absorption correction	Semi-empirical
Min./max. transmission	0.7040/0.7654
Solution and refinement	
Solution and refinement	Sigmons SUELVIL DI US
System used	(VMS)
Solution	(VIND) Direct methods
Befinement method	Full metrix least squares
Quantity minimized	$\sum w(F - F)^2$
Undrogen stoms	$2w(r_0 - r_c)$ Biding model fixed isotropic <i>II</i>
Weighting scheme	$m^{-1} = \sigma^2(F) \pm 0.0026F^2$
Number of parameters	w = 0 (r) + 0.0020r
refined	517
Final R indices (all data)	R = 8.22% w $R = 7.42%$
R indices (6a data)	R = 3.93% w $R = 5.44%$
Goodness-of-fit	0.89
Largest and mean $\Delta/\sigma$	0.001, 0.000
Data-to-parameter ratio	8.8:1
Largest difference peak	$0.76 \text{ e}\text{\AA}^{-3}$
Largest difference hole	-0.83 eÅ <sup>-3</sup>
<b>-</b>	

Table 1. Experimental data for the crystal structure analysis of  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$ 

		<i>x</i>	у	z	U(eq) <sup>a</sup>
$\begin{array}{llllllllllllllllllllllllllllllllllll$	I(1)	10623(1)	5923(1)	3104(1)	57(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	I(2)	4423(1)	-64(1)	6959(1)	59(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P(1)	180(3)	575(3)	2884(3)	44(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P(2)	4909(3)	4546(3)	-2886(3)	45(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1)	648(8)	914(7)	3643(6)	53(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2)	4552(9)	5357(7)	-3670(7)	62(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(11)	1330(12)	-66(10)	2020(10)	45(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12)	1067(15)	-734(13)	1430(11)	69(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(13)	1988(23)	-1231(15)	821(14)	105(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(14)	3225(20)	-1048(16)	769(13)	89(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(15)	3481(16)	-421(15)	1343(13)	74(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(16)	2526(16)	34(12)	1992(11)	70(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(21)	-298(11)	1794(11)	2122(9)	44(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(22)	258(14)	2856(13)	1974(11)	65(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(23)	-124(17)	3836(12)	1439(13)	78(9)
$\begin{array}{ccccccc} C(25) & -1637(15) & 2670(15) & 1214(13) & 79(9) \\ C(26) & -1273(13) & 1719(12) & 1754(10) & 53(7) \\ C(31) & -1155(11) & -438(10) & 3432(9) & 49(6) \\ C(32) & -958(11) & -1408(10) & 4242(9) & 45(6) \\ N(33) & -2092(8) & -2179(8) & 4856(7) & 43(5) \\ C(34) & -2605(12) & -2732(11) & 4224(10) & 55(6) \\ C(35) & -3052(12) & -1539(11) & 5464(10) & 58(6) \\ C(36) & -1673(12) & -3118(10) & 5591(9) & 51(6) \\ C(41) & 3669(12) & 3525(10) & -2078(8) & 39(6) \\ C(42) & 2462(13) & 3823(13) & -2008(11) & 61(7) \\ C(43) & 1500(16) & 3073(20) & -1341(14) & 91(10) \\ C(44) & 1674(17) & 2107(17) & -771(14) & 78(9) \\ C(45) & 2835(19) & 1777(14) & -850(13) & 84(9) \\ C(46) & 3815(14) & 2505(13) & -1485(12) & 73(8) \\ C(51) & 5415(12) & 5261(12) & -2086(9) & 49(6) \\ C(52) & 5059(14) & 6365(13) & -2052(12) & 69(8) \\ C(53) & 5420(22) & 6966(17) & -1444(17) & 99(11) \\ C(54) & 6163(22) & 6508(24) & -948(18) & 113(13) \\ C(55) & 6509(15) & 5433(22) & -923(13) & 93(10) \\ C(56) & 6153(13) & 4767(13) & -1495(11) & 62(7) \\ C(61) & 6183(11) & 3736(11) & -3423(9) & 48(6) \\ C(62) & 5953(10) & 3189(10) & -4232(9) & 36(5) \\ N(63) & 7085(8) & 2780(8) & -4898(7) & 34(4) \\ C(64) & 6656(12) & 2221(11) & -5606(10) & 57(6) \\ C(65) & 7633(12) & 1879(11) & -4305(11) & 58(7) \\ C(66) & 8024(12) & 3720(11) & -5518(10) & 57(6) \\ \end{array}$	C(24)	-1033(16)	3735(14)	1060(11)	69(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(25)	-1637(15)	2670(15)	1214(13)	79(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(26)	-1273(13)	1719(12)	1754(10)	53(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(31)	-1155(11)	-438(10)	3432(9)	49(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(32)	-958(11)	-1408(10)	4242(9)	45(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(33)	-2092(8)	-2179(8)	4856(7)	43(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(34)	-2605(12)	-2732(11)	4224(10)	55(6)
$\begin{array}{cccccccc} C(36) & -1673(12) & -3118(10) & 5591(9) & 51(6) \\ C(41) & 3669(12) & 3525(10) & -2078(8) & 39(6) \\ C(42) & 2462(13) & 3823(13) & -2008(11) & 61(7) \\ C(43) & 1500(16) & 3073(20) & -1341(14) & 91(10) \\ C(44) & 1674(17) & 2107(17) & -771(14) & 78(9) \\ C(45) & 2835(19) & 1777(14) & -850(13) & 84(9) \\ C(46) & 3815(14) & 2505(13) & -1485(12) & 73(8) \\ C(51) & 5415(12) & 5261(12) & -2086(9) & 49(6) \\ C(52) & 5059(14) & 6365(13) & -2052(12) & 69(8) \\ C(53) & 5420(22) & 6966(17) & -1444(17) & 99(11) \\ C(54) & 6163(22) & 6508(24) & -948(18) & 113(13) \\ C(55) & 6509(15) & 5433(22) & -923(13) & 93(10) \\ C(56) & 6153(13) & 4767(13) & -1495(11) & 62(7) \\ C(61) & 6183(11) & 3736(11) & -3423(9) & 48(6) \\ C(62) & 5953(10) & 3189(10) & -4232(9) & 36(5) \\ N(63) & 7085(8) & 2780(8) & -4898(7) & 34(4) \\ C(64) & 6656(12) & 2221(11) & -5606(10) & 57(6) \\ C(65) & 7633(12) & 1879(11) & -4305(11) & 58(7) \\ C(66) & 8024(12) & 3720(11) & -5518(10) & 57(6) \\ \end{array}$	C(35)	-3052(12)	-1539(11)	5464(10)	58(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(36)	-1673(12)	-3118(10)	5591(9)	51(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(41)	3669(12)	3525(10)	-2078(8)	39(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(42)	2462(13)	3823(13)	-2008(11)	61(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(43)	1500(16)	3073(20)	-1341(14)	91(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(44)	1674(17)	2107(17)	-771(14)	78(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(45)	2835(19)	1777(14)	-850(13)	84(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(46)	3815(14)	2505(13)	-1485(12)	73(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(51)	5415(12)	5261(12)	-2086(9)	49(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(52)	5059(14)	6365(13)	-2052(12)	69(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(53)	5420(22)	6966(17)	-1444(17)	99(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(54)	6163(22)	6508(24)	-948(18)	113(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(55)	6509(15)	5433(22)	-923(13)	93(10)
C(61)      6183(11)      3736(11)      -3423(9)      48(6)        C(62)      5953(10)      3189(10)      -4232(9)      36(5)        N(63)      7085(8)      2780(8)      -4898(7)      34(4)        C(64)      6656(12)      2221(11)      -5606(10)      57(6)        C(65)      7633(12)      1879(11)      -4305(11)      58(7)        C(66)      8024(12)      3720(11)      -5518(10)      57(6)	C(56)	6153(13)	4767(13)	-1495(11)	62(7)
C(62)      5953(10)      3189(10)      -4232(9)      36(5)        N(63)      7085(8)      2780(8)      -4898(7)      34(4)        C(64)      6656(12)      2221(11)      -5606(10)      57(6)        C(65)      7633(12)      1879(11)      -4305(11)      58(7)        C(66)      8024(12)      3720(11)      -5518(10)      57(6)	C(61)	6183(11)	3736(11)	-3423(9)	48(6)
N(63) 7085(8) 2780(8) -4898(7) 34(4) C(64) 6656(12) 2221(11) -5606(10) 57(6) C(65) 7633(12) 1879(11) -4305(11) 58(7) C(66) 8024(12) 3720(11) -5518(10) 57(6)	C(62)	5953(10)	3189(10)	-4232(9)	36(5)
$\begin{array}{ccccc} C(64) & 6656(12) & 2221(11) & -5606(10) & 57(6) \\ C(65) & 7633(12) & 1879(11) & -4305(11) & 58(7) \\ C(66) & 8024(12) & 3720(11) & -5518(10) & 57(6) \\ \end{array}$	N(63)	7085(8)	2780(8)	-4898(7)	34(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(64)	6656(12)	2221(11)	-5606(10)	57(6)
C(66) = 8024(12) = 3720(11) = -5518(10) = 57(6)	C(65)	7633(12)	1879(11)	-4305(11)	58(7)
	C(66)	8024(12)	3720(11)	-5518(10)	57(6)

<sup>a</sup> Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

# Discussion

The labeling of atoms is shown in Fig. 1. Intramolecular distances and angles are collected in Tables 3 and 4.

The crystallographic asymmetric unit consists of two independent  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+]$ 

Table 2. Final atomic coordinates  $(\times 10^4)$  and equivalent isotropic displacement coefficients ( $Å^2 \times 10^3$ ) for  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$ 



Fig. 1. Labeling of atoms in the crystallographic asymmetric unit of  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$ (ORTEP2 diagram; 30% probability envelopes for nonhydrogen atoms).

cations ("cation 1" associated with P(1)=O(1) and "cation 2" associated with P(2)=O(2)) and two [I<sup>-</sup>] anions. The packing of these species within the unit cell is illustrated in Figs. 2 and 3. The most important interionic contacts (see Table 5) involve hydrogen bonding from either the oxygen atoms of the P=O groups or the iodide anions to C-H linkages on surrounding  $-N(CH_3)_3^+$ ,  $-C_6H_5$  or  $-CH_2$ - moieties. The oxygen atoms interact principally with hydrogen atoms of the  $-N(CH_3)_3^+$  function. The shortest of these interactions are O(1)…H(32A) [-x, -y, 1 - z] =2.42Å and O(1)…H(36C) [-x, -y, 1 - z] = 2.55Åfor cation 1; and O(2)…H(64C) [1 - x, 1 - y, -1 - z]

**Table 3.** Interatomic distances (Å) for  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^*][I^-]$ 

Cation 1		Cation 2	
P(1) = O(1)	1.47(1)	P(2) - O(2)	1.47(1)
P(1) - C(11)	1.79(1)	P(2) - C(41)	1.79(1)
P(1) - C(21)	1.81(1)	P(2) - C(51)	1.78(2)
P(1) - C(31)	1.81(1)	P(2) - C(61)	1.80(1)
C(31) - C(32)	1.52(2)	C(61) - C(62)	1.53(2)
C(32) - N(33)	1.50(1)	C(62) - N(63)	1.49(1)
N(33)-C(34)	1.47(2)	N(63) - C(64)	1.51(2)
N(33)-C(35)	1.49(2)	N(63)-C(65)	1.48(2)
N(33)-C(36)	1.55(2)	N(63)-C(66)	1.48(1)

**Table 4.** Bond angles (°) for  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$ 

Cation 1	Cation 1 Cation 2		
(A) Angles around phosphorus atoms			
O(1) - P(1) - C(11)	111.8(6)	O(2) - P(2) - C(41)	112.7(6)
O(1) - P(1) - C(21)	111.9(6)	O(2) - P(2) - C(51)	112.0(6)
O(1) - P(1) - C(31)	113.5(5)	O(2) - P(2) - C(61)	112.4(6)
C(11) - P(1) - C(21)	106.7(6)	C(41) - P(2) - C(51)	107.1(6)
C(11) - P(1) - C(31)	106.9(6)	C(41) - P(2) - C(61)	106.8(6)
C(21) - P(1) - C(31)	105.6(6)	C(51)-P(2)-C(61)	105.3(7)
(B) Phosphorus-carb	on-carbor	angles	
P(1)-C(11)-C(12)	124(1)	P(2) - C(41) - C(42)	118(1)
P(1)-C(11)-C(16)	119(1)	P(2)-C(41)-C(46)	125(1)
P(1)-C(21)-C(22)	119(1)	P(2) - C(51) - C(52)	118(1)
P(1)-C(21)-C(26)	123(1)	P(2)-C(51)-C(56)	124(1)
P(1)-C(31)-C(32)	111(1)	P(2)-C(61)-C(62)	112(1)
(C) Angles within the $-CH_2NMe_1^+$ mojety			
C(31) - C(32) - N(33)	114.4(11)	C(61) - C(62) - N(63)	114.1(10)
C(32)-N(33)-C(34)	112.4(9)	C(62) - N(63) - C(64)	105.9(9)
C(32) = N(33) = C(35)	110.8(9)	C(62) = N(63) = C(65)	111.6(8)
C(32) = N(33) = C(36)	105.7(9)	C(62) - N(63) - C(66)	113.1(9)
C(34) - N(33) - C(35)	110.1(10)	C(64) - N(63) - C(65)	106.8(10)
C(34) - N(33) - C(36)	108.8(9)	C(64) - N(63) - C(66)	108.4(9)
C(35)-N(33)-C(36)	108.8(9)	C(65)-N(63)-C(66)	110.6(10)



Fig. 2. Packing diagram for  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+]$ [I<sup>-</sup>], projected on (100); note hydrogen bonding from the oxygen atoms of the P=O groups to neighboring H-C systems.



Fig. 3. Packing diagram for  $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3)^+][I^-]$ , projected on (010).

Table 5. Interionic contacts involving the iodide anion and oxygen atoms (based upon the "X-ray determined" C-H distance of 0.96 Å)<sup>11</sup>

Atom-Atom [symcode] <sup>a</sup>	Dist, Å
I(1)…H(34B) [1665]	3.11
I(1)…H(32B) [1665]	3.16
I(1)…H(61B) [2765]	3.18
I(1)…H(36B) [1665]	3.20
I(1)…H(65A) [2765]	3.32
I(1)…H(43A) [2665]	3.33
I(2)…H(26A) [2556]	3.10
I(2)…H(65B) [1556]	3.12
I(2)····H(62B) [1556]	3.16
I(2)…H(64B) [1556]	3.29
I(2)…H(31B) [2556]	3.35
I(2)····H(34A) [2556]	3.35
O(1)…H(32A) [2556]	2.42
O(1)…H(36C) [2556]	2.55
O(2)…H(64C) [2664]	2.44
O(2)…H(62A) [2664]	2.46

<sup>a</sup> The symmetry code (symcode) is in the standard abbreviated ORTEP format, in which the first digit represents an equipoint of the space group (for P1: 1 = x, y, z; 2 = -x, -y, -z) and the second through fourth digits represent unit cell translations along  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$  (respectively) relative to the code 555, which corresponds to the defined basic unit cell.

= 2.44Å and O(2)···H(62C) [1 - x, 1 - y, -1 - z]= 2.46Å for cation 2. The iodide ions are associated with I···H contacts as short as 3.10Å. The shortest interaction to I(1) involves a hydrogen atom from an  $-N(CH_3)_3^+$  group (I(1)···H(34B) [1 + x, 1 + y, z] =3.11Å); the shortest to I(2) involves, instead, a hydrogen atom from a phenyl group (I(2)···H(26A) [-x, -y, 1 - z] = 3.10Å).

# The $[(C_6H_5)_2P(=O)(CH_2CH_2N(CH_3)_3^+]$ cations

The phosphine oxide linkages are equivalent, with P(1)=O(1) = 1.47(1)Å in cation 1 and P(2)=O(2) = 1.47(1)Å in cation 2. These may be compared with such values of 1.484Å in  $(C_6H_5)_3PO$ ,<sup>12</sup> and 1.482(3)Å in  $(p-CH_3C_6H_4)_3PO \cdot 1/2(H_2O)$ .<sup>13</sup>

The O=P-C angles are all expanded from the regular tetrahedral angle of 109.5°, with values of 111.8(6)°-113.5(5)° in cation 1 and 112.0(6)°-112.7(6)° in cation 2 (overall average  $\angle O=P-C = 112.4^{\circ}$ ); the C-P-C angles are correspondingly contracted, with values of 105.6(6)°-106.9(6)° in cation 1 and 105.3(7)°-107.1(6)° in cation 2 (overall average  $\angle C-P-C = 106.4^{\circ}$ ). P-C<sub>6</sub>H<sub>5</sub> distances range from 1.78(2)Å through 1.81(1)Å (average = 1.795Å), while

the P-CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sup>+</sup> bond lengths are 1.81(1)Å in cation 1 and 1.80(1)Å in cation 2 (average = 1.805Å). Carbon-carbon distances within the four phenyl groups are of relatively low precision (due to the presence of the two "heavy" iodide ions, Z = 53, in the asymmetric unit); individual values range from 1.31(3)Å to 1.41(2)Å, averaging 1.37Å. There is clearly some artificial librational shortening of the outermost C(meta) - C(para) bond lengths. (Note the large U(eq) values for C(14), C(24), C(44), and C(54) (see Table 2). Angles within the phenyl groups show the expected pattern, with reduced values at the *ipso* carbons<sup>14,15</sup> [C(12)-C(11)-C(16)] $117(1)^{\circ}$ , C(22)-C(21)-C(26) = 118(1)°,  $C(42)-C(41)-C(46) = 118(1)^{\circ}$ and C(52) - $C(51) - C(56) = 119(2)^{\circ}$ ].

The quaternary ammonium ions have the expected tetrahedral geometry and are associated with  $N-CH_2CH_2P(C_6H_5)_2$  bond lengths of 1.52(2)Å and 1.53(2)Å and with  $N-CH_3$  linkages ranging from N(33)-C(34) = 1.47(2)Å to N(33)-C(36) = 1.55(2)Å (average N-Me = 1.50Å).

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## References

- Smith, R.T.; Baird, M.C. Transition Met. Chem. (Weinheim, Ger.), 1981, 6, 197.
- 2. Markiewicz, M.K.; Baird, M.C. Inorg. Chim. Acta 1986, 113, 95.
- Peiffer, G.; Chan, S.; Pendayan, A.; Waegell, B.; Zahra, J. J. Mol. Catal. 1990, 59, 1.
- Rominger, R.L., Ph.D. Thesis, 1996, State University of New York at Buffalo; see pp 43-50.
- 5. Smith, R.T.; Baird, M.C. Inorg. Chim. Acta 1982, 62, 135.
- Churchill, M.R.; Lashewycz, R.A.; Rotella, F.J. Inorg. Chem. 1977, 16, 265.
- Nowacki, W.; Matsumoto, T.; Edenharter, A. Acta Crystallogr. 1967, 22, 935.
- Sheldrick, G.M. SHELXTL PLUS; Siemens Analytical Instruments; Madison, WI, 1989.
- Sheldrick, G.M. SHELXTL PLUS. An integrated system for solving, refining and displaying crystal structures from diffraction data, For Nicolet R3m/V; University of Göttingen: Germany, 1987.
- International Tables for X-Ray Crystallography, Volume IV; Kynoch Press: Birmingham, England, 1974: (a) pp 99-101; (b) pp 149-150.
- 11. Churchill, M.R. Inorg. Chem. 1973, 12, 1213.
- 12. Spek, A.L. Acta Cryst. Section C 1987, C43, 1233.
- 13. Churchill, M.R.; See, R.F.; Randall, S.L.; Atwood, J.A. Acta Cryst. Section C 1993, C49, 345 (and references therein).
- Churchill, M.R.; DeBoer, B.G. Inorg. Chem. 1975, 14, 2630.
  Dominicano, A.; Vaciago, A.; Coulson, C.A. Acta Cryst. Section B 1975, B31, 1630.