

# STRUCTURAL STUDY ON QUASI-PHOSPHONIUM SALTS CONTAINING PHOSPHORUS–OXYGEN, PHOSPHORUS–NITROGEN AND PHOSPHORUS–SULPHUR BONDS

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**The crystal and molecular structures of six quasi-phosphonium salts containing phosphorus–heteroatom (heteroatom = oxygen, sulphur or nitrogen) bonds were determined. Comparison of the molecular parameters obtained with those available for reference structures demonstrated that the ‘double bond’ character for the  $P^+—Y$  bond decreases in the order  $Y = N \gg O > S$ .**

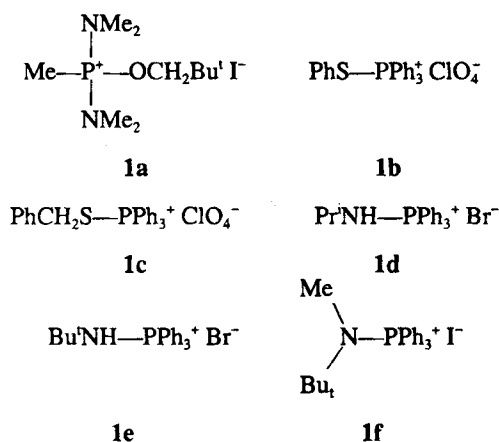
## INTRODUCTION

Quasi-phosphonium ions, defined as phosphonium structures in which the phosphorus atom is bonded directly to at least one heteroatom (O, N, S, etc.), are important species because of their reactivity and their role as intermediates in various organophosphorus reactions.<sup>1</sup> The nature of the phosphorus–heteroatom bonding in these systems is therefore of interest, as it should have a direct bearing on their chemical behaviour. Single-crystal x-ray diffraction measurements carried out previously on the alkoxyphosphonium ions,  $(RO)_nPR'_{4-n}^+$  ( $n = 1, 2, 3$ ) demonstrated that there is little, if any, double bond character in the  $P^+—Ph$  bond ( $R' = Ph$ ), but the  $P^+—O$  bonds show some double bond character with  $p_\pi-d_\pi$  back-donation from oxygen to phosphorus.<sup>2</sup> Considerably less information is available on the bonding parameters of quasi-phosphonium ions containing the  $P^+—S$  and  $P^+—N$  bonds. Since our recent studies demonstrated a significant difference in the photochemical behaviour of the ‘classical’ quaternary phosphonium<sup>3</sup> and alkylthio- (or arylthio-) phosphonium<sup>4</sup> ions, we decided to determine structural features of some quasi-phosphonium salts containing different phosphorus–heteroatom bonds. It was hoped that the molecular parameters, particularly bond distances and bond angles, would provide useful information about the nature of the bonding of those systems.

## RESULTS AND DISCUSSION

Six quasi-phosphonium salts (**1**), one containing two  $P—N$  bonds and one  $P—O$  bond (**1a**), two containing one  $P—S$  bond (**1b, c**) and three aminophosphonium salts containing one  $P—N$  bond (**1d, e, f**) (Scheme 1), were prepared and single-crystal x-ray diffraction structure determinations were performed. All salts were sufficiently stable to allow data collection to be carried without the need for special precautions to exclude atmospheric moisture. Principal molecular parameters, including the  $P^+ \cdots X^-$  non-bonded distances, are given in Table 1 and the perspective (ORTEP<sup>5</sup>) views of the molecules are given in Figure 1.

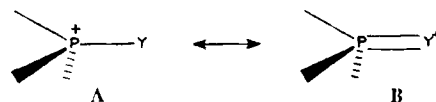
The first obvious conclusion is that all substrates **1** are tetracoordinate phosphonium salts with no indication of a pentacoordinate (phosphorane) structure. In all salts the phosphorus atom is perfectly tetrahedral with a remarkably constant value of the average  $Y—P—Z$  angle. Irrespective of the nucleophilicity of the counterion, the non-bonded  $P^+ \cdots X^-$  distances are well above the corresponding sum of the van der Waal's radii with no evidence for even an ‘early stage’ of the formation of the *tbp* structure. The phosphorus–heteroatom bonding, on the other hand, shows interesting variations within the tetrahedral structure of the phosphonium ions. The observed  $P^+—heteroatom$  bond distances should be discussed in relation to the ‘pure’



Scheme 1

single and 'pure' double bonds between phosphorus and a given heteroatom. Such a comparison will depend, of course, on the models chosen to represent a typical 'single' and 'double' bonding at phosphorus. Although the exact value of a bond length depends on such factors as the electronegativities and steric effects of the remaining substituents, the interaction of the neighbouring molecules and crystal structure effects,<sup>6</sup> the typical ranges of the P—O(C), P=O, P—S and P=S bond distances are available in the literature. As far as the P—N bond is concerned, the value for the 'pure' single bond was taken from the dipolar molecule of phosphoramidic acid  $\text{H}_3\text{N}^+ - \text{PO}_3\text{H}^-$  (1.78 Å<sup>7</sup>), while the value for the 'double' bond was taken from the molecular structure of *N-tert-butyl-P,P,P*-triphenylphosphine

imide,  $\text{Ph}_3\text{P}=\text{NBu}^+$  (2), determined in our laboratory and taken as a model closely related to the ionic substrates 1d, e and f. A comparison of the phosphorus–heteroatom bond distances observed for ions 1 with the limiting values accepted for the corresponding single and double bonds is given in Table 2. Assuming that the correlation between bond length and bond order<sup>9</sup> operates for ions 1, Table 2 reveals interesting differences between individual heteroatoms. All observed phosphorus–heteroatom bond distances are intermediate between the corresponding values for a single and a double bond, but the exact location within that range varies from heteroatom to heteroatom. If the structure of a quasi-phosphonium ion can also be represented by two resonance structures, A and B (Scheme 2), the degree of the  $p_\pi-d_\pi$  back-donation from the heteroatom to phosphonium centre can be measured by the value of the 'shortening' of the 'pure' single bond to the observed value.



Scheme 2.

Relative to the 'pure' single bond, the phosphorus–oxygen, phosphorus–nitrogen and phosphorus–sulphur distances in the quasi-phosphonium ions studied in this and previous<sup>2</sup> work are shortened by 32%, 62% and 26%, respectively. Thiophosphonium ions 1b and c can be compared directly with triphenylphosphine sulphide, as the products of 'S-phenylation' (or 'S-benylation') of that substrate. The P=S bond distance in  $\text{Ph}_3\text{PS}$  is 1.950(3) Å,<sup>10</sup> and our

Table 1. X-ray crystallographic data for quasi-phosphonium salts 1

Parameter	1a	1b	1c	1d	1e	1f
Bond distances (Å):						
P—Ph (av.)		1.789(4)	1.781(4)	1.784(9)	1.800(6)	1.800(4)
P—O	1.546(7)					
P—N	1.595(10) <sup>a</sup>			1.628(7)	1.621(3)	1.646(3)
P—S		2.074(2)	2.050(1)			
Bond angles (°):						
P—O—C	121.6(8)					
P—N—C	121.1(3) <sup>b</sup>					
P—S—C		100.1(2)	105.6(1)	124.2(8)	129.1(2)	121.3(3) <sup>a</sup>
C—N—C	113(1) <sup>a</sup>					115.2(3)
Y—P—Z (av.)	109.5(5)	109.5(2)	109.5(1)	109.5(4)	109.4(1)	109.4(2)
P <sup>+</sup> ...X <sup>-</sup> non-bonded distance (Å)	4.987	5.237 <sup>c</sup>	6.063 <sup>c</sup>	4.287	4.173	5.853

<sup>a</sup> Average of two values.

<sup>b</sup> Average of four values.

<sup>c</sup> P...Cl distance.

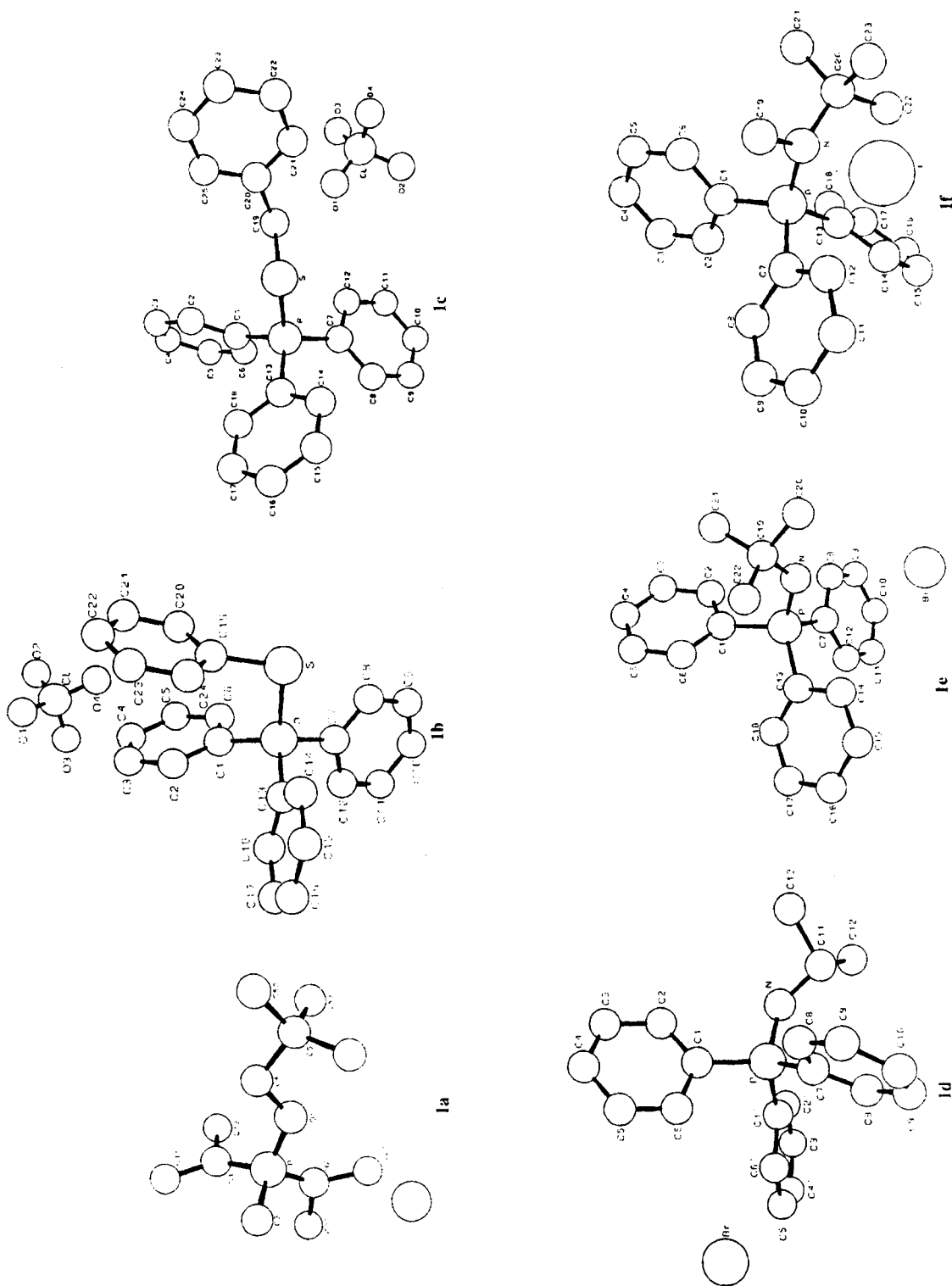
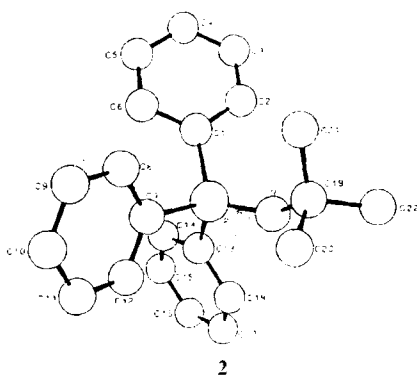


Figure 1. Perspective (ORTEP) views of the molecules



Compound 2.

Table 2. Comparison of phosphorus-heteroatom bond distances (Å)

Heteroatom in the P-heteroatom bond	Single	Double	Observed for 1
O	1.590(16) <sup>a</sup>	1.467(7) <sup>a</sup>	1.551(9) <sup>b</sup>
N	1.78 <sup>c</sup>	1.543(2) <sup>d</sup>	1.632(4) <sup>e</sup>
S	2.10(5) <sup>f</sup>	1.954(5) <sup>g</sup>	2.062(1) <sup>h</sup>

<sup>a</sup> Taken from Ref. 8.<sup>b</sup> Taken from Ref. 2. Compound **1a** was excluded since it contains two additional phosphorus-heteroatom bonds (P—N), and is discussed separately.<sup>c</sup> Taken from Ref. 7.<sup>d</sup> This work.<sup>e</sup> Average for **1d**, **e** and **f**; **1a** was excluded (see footnote b).<sup>f</sup> Taken from Ref. 6; average of a series P—S distances.<sup>g</sup> Average for **1b** and **c**.

results clearly show that the substitution at sulphur is followed by a significant change in the nature of the phosphorus-sulphur bond, giving a mean P—S bond length of 2.062 Å in **1b** and **c**. In other words, the contribution of the resonance structure B to the structure of the ions decreases in the order Y = N ≫ O > S. The bond distances data correlate well with the P—Y—C bond angles values. For Y = N, the average value (Table 1) is 123.9 ± 3.7°, clearly suggesting sp<sup>2</sup> hybridization of the nitrogen. In agreement with that, the tertiary nitrogen in **1f** (the average bond angle at N is 119.3°) is almost completely planar, with the deviation from the plane determined by phosphorus and two alkyl carbons of only 0.129(3) Å. Similarly, the bond angles at oxygen, although varying from structure to structure,<sup>2</sup> are never below the value of 120°.

In contrast with the oxygen and nitrogen analogues, alkylthio (thioaryl) phosphonium salts are characterised not only by a 'long' P-heteroatom bond, but also by the

P<sup>+</sup>—S—C bond angles well below the tetrahedral value (the average value for **1b** and **1c** is 102.9 ± 3.9°), indicating that the bonding at sulphur is not much different from that observed for hydrogen sulphide and its simple derivatives.

The ion **1a** contains two types of phosphorus-heteroatom bond (one P<sup>+</sup>—O and two P<sup>+</sup>—N) at the phosphonium centre. The bonding parameters (distances and angles) are, however, very similar to those observed for ions in which only one type of P-heteroatom bond is present (Tables 1 and 2). Indeed, as far as the P<sup>+</sup>—O compounds are concerned, the length of this bond remains approximately constant not only as the groups on P are changed but also as the organic group attached to oxygen is changed from alkyl to aryl. The P—O bond distance in **1a** (1.546 Å) is very similar to the average value of 1.551 Å observed for various R<sub>n</sub>P(OR')<sub>4-n</sub><sup>+</sup> (R, R' = alkyl or aryl; n = 0, 1, 2) salts.<sup>2b</sup> It has been shown that even the presence of strongly electron-withdrawing substituents, as in methyl tri(*p*-nitrophenoxy)phosphonium chloride, does not have any noticeable effect on the P—O bond distance (1.552-Å).<sup>11</sup> It seems, therefore, that the nature of the P<sup>+</sup>—Y bond in a quasi-phosphonium system depends primarily on the nature of Y, and not on the remaining substituents at phosphorus.

## EXPERIMENTAL

NMR spectra were recorded on a Bruker AC300 spectrometer and chemical shifts are given in δ (ppm) relative to tetramethylsilane as an internal standard (<sup>1</sup>H) or 85% H<sub>3</sub>PO<sub>4</sub> as an external standard (<sup>31</sup>P). Melting points are uncorrected.

**Quasi-phosphonium salts (1).** Neopentyloxy(bisdimethylamino)methylphosphonium iodide (**1a**) was prepared as described before.<sup>12</sup> Yield 81%; m.p. 144 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 1.01 (s, 9H), 2.35 (d, 3H, J = 13.8 Hz), 2.89 (d, 12H, J = 9.6 Hz), 3.91 (d, 2H, J = 4.2 Hz); <sup>31</sup>P NMR, δ 59.6.

**Thiophenoxy- (1b) and thiobenzyloxy- (1c) triphenylphosphonium perchlorate.** These were prepared electrochemically according to the literature procedure.<sup>13</sup> Compound **1b**, yield 50%; m.p. 174–175 °C (lit.<sup>13</sup> m.p. 172–173 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 7.17–7.43 (m, 4H), 7.39–7.49 (m, 1H), 7.55–7.84 (m, 15H); <sup>31</sup>P NMR, δ 36.2. Compound **1c**, yield 60%; m.p. 141–142 °C (lit.<sup>13</sup> m.p. 141–142 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 4.14 (d, 2H, J = 10.8 Hz), 7.12–7.28 (m, 5H), 7.71–7.88 (m, 15H); <sup>31</sup>P NMR, δ 44.7.

**(Alkylamino)triphenylphosphonium bromides (1d–f).** These were prepared according to the literature procedure.<sup>14</sup> Compound **1d**, yield 54%; m.p. 240–242 °C (lit.<sup>14</sup> m.p. 242–243 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 1.33 (d, 6H, J = 6.8 Hz), 3.15 (m, 1H),

Table 3. Crystallographic data acquisition and refinement details

Parameter	1a	1b	1c	1d	1e	1f	2
Empirical formula	$C_{20}H_{28}IN_2OP$	$C_{26}H_{20}PSClO_4$	$C_{25}H_{22}PSClO_4$	$C_{21}H_{23}NPBr$	$C_{22}H_{25}NPBr$	$C_{22}H_{27}PNI$	$C_{22}H_{24}PN$
Molecular weight	350.22	470.91	484.94	400.30	414.33	475.35	333.42
Crystal dimensions (mm)	0.22×0.31×0.35	0.31×0.55×0.60	0.22×0.23×0.55	0.31×0.33×0.53	0.28×0.40×0.55	0.21×0.25×0.32	0.20×0.30×0.51
Space group	$C2/c$	$P2_1/n$	$P_1$	$Pcmn$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Cell dimensions:							
$a$ (Å)	18.031(3)	12.118(2)	9.981(3)	16.831(2)	8.659(2)	8.927(1)	9.827(1)
$b$ (Å)	17.440(3)	11.794(2)	13.170(2)	13.346(3)	13.465(2)	10.113(1)	20.286(2)
$c$ (Å)	11.356(2)	16.121(3)	19.160(2)	8.949(1)	13.492(1)	24.125(2)	10.353(1)
$\alpha$ (°)	90	90	101.86(1)	90	90	90	90
$\beta$ (°)	111.99(2)	93.83(1)	101.71(2)	90	98.19(11)	90.13(2)	110.94(1)
$\gamma$ (°)	90	90	100.77(2)	90	90	90	90
$Z$	8	4	2	4	4	4	4
Volume (Å <sup>3</sup> )	3311.3	2298.8(7)	2343.7(8)	2010.1(5)	2019.6(5)	2178.0(4)	1927.5(4)
$D$ (calc) (g cm <sup>-3</sup> )	1.397	1.361	1.374	1.323	1.363	1.449	1.149
$\mu$ (cm <sup>-1</sup> )	19.9	3.6	3.4	2.1	2.1	15.2	1.4
$F(000)$	1424	976	1008	824	888	964	712
Scan type ( $\omega : 2\theta$ )	1:1	1:1	1:1	1:1	1:1	1:1	1:1
Scan Range ( $\theta^\circ$ )	$3 < \theta < 25$	$3 < \theta < 30$	$3 < \theta < 30$	$3 < \theta < 30$	$3 < \theta < 30$	$3 < \theta < 30$	$3 < \theta < 30$
Zone collected:							
$h$	-19, +19	0, +17	0, +14	0, +23	-12, 0	-12, +12	-13, +13
$k$	0, +20	0, +16	-18, +18	-18, 0	-14, 0	0, +28	-18, +18
$l$	0, +13	-22, +22	-27, +27	0, +12	-34, 0	0, +14	-27, +27
Max. scan speed (deg min <sup>-1</sup> )	3.0 (constant)	5.49	5.49	5.49	5.49	5.49	5.49
Max. scan time (s)	80	60	60	60	60	60	60
Scan angle ( $\omega + 0.34 \tan \theta$ ) (°)	$\omega = 0.80$						
Aperture size (mm)	(constant)	0.51	0.51	0.61	0.52	0.73	0.56
Reflections collected	1.0×1.0	1.3×4.0	1.3×4.0	1.3×4.0	1.3×4.0	1.3×4.0	1.3×4.0
Decay (%)	Not recorded	7251	13600	3326	6388	6782	6027
EAC correction factor:	<2.0	-1.0	-1.8	-0.9	-1.4	+0.1	-0.8
Maximum	Not used	1.000	1.000	1.000	1.000	1.000	1.000
Minimum		0.963	0.946	0.936	0.929	0.970	0.964
Average		0.984	0.973	0.958	0.970	0.987	0.982
Unique reflections used (>3 $\sigma$ (I))	1757	3903	7453	1355	3849	3978	3346
Parameters refined	86	281	356	117	303	248	290
Max. positional shift (esd)	0.10	0.007	0.096	0.317	0.016	0.043	0.042
Residual electron density (e Å <sup>-3</sup> ):							
Maximum	1.021	0.631	0.529	0.957	0.398	0.999	0.368
Minimum	-0.926	-0.769	-0.402	-0.825	-0.636	-1.002	-0.284
$U_{iso}(H)$ (Å <sup>2</sup> )	0.12	0.103(4)	0.073(3)	0.130(9)	0.063(2)	0.078(3)	0.084(2)
Refinement of H atoms <sup>a</sup>	All fixed	All fixed	All experimental	All fixed	All experimental	All fixed	All experimental
$R$	0.0477	0.0821	0.0608	0.0769	0.0465	0.0451	0.0577
$R_w$ [ $w = \sigma^{-2}(F_o)$ ]	0.0501	0.0627	0.0404	0.0530	0.0307	0.0297	0.0392

<sup>a</sup> Fixed in calculated positions and included in the refinement with a common isotropic thermal parameter, or refined in experimentally determined positions with a common isotropic thermal parameter, that was also refined.

7.55–7.89 (m, 15H);  $^{31}\text{P}$  NMR,  $\delta$  36.4. Compound **1e**, yield 95%; m.p. 223–225 °C (lit.<sup>14</sup> m.p. 223 °C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  1.32 (s, 9H), 7.44 (d, 1H,  $J=6.2$  Hz), 7.57–7.98 (m, 15H);  $^{31}\text{P}$  NMR,  $\delta$  32.0. Compound **1f**, yield 79%; m.p. 215–216 °C (lit.<sup>14</sup> m.p. 214–215 °C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  1.34 (s, 9H), 2.92 (d, 3H,  $J=10.8$  Hz), 7.73–7.88 (m, 15H);  $^{31}\text{P}$  NMR,  $\delta$  43.6.

*tert*-Butyliminotriphenylphosphorane (**2**). This was prepared according to the literature procedure.<sup>14</sup>

*Crystal structure determination.* Diffraction-quality crystals of **1a–f** and **2** were obtained by standard crystallization methods. All diffraction measurements were obtained at room temperature and the data were collected on Philips PW1100 (**1a**) and Enraf Nonius CAD4 (**1b–f**) diffractometers with  $\text{Mo K}\alpha$  radiation (graphite monochromator,  $\lambda=0.7107$  Å). Accurate unit cell parameters were obtained by least-squares methods from the position of 25 selected centred reflections for each crystal (Table 3). There was no significant crystal decay and intensities were corrected for absorption, as indicated in Table 3, and also for Lorentz and polarization effects. Standard intensity checks and orientation control were carried out.

The structures were solved by Patterson and direct methods.<sup>15,16</sup> All non-hydrogen atoms for **1b–f** and **2** and the non-carbon and non-hydrogen atoms for **1a** were refined anisotropically. The hydrogen atoms were placed in either experimentally determined or in idealized positions, and included in the refinement with common isotropic thermal parameters, as indicated in Table 3.

Perspective views of the molecules, prepared with ORTEP,<sup>5</sup> are represented in Figure 1, illustrating the crystallographic numbering schemes used. Atomic scattering factors were taken from the literature.<sup>17</sup>

Supplementary material (atom coordinates, bond lengths and angles and thermal parameters) are available from the authors.

#### ACKNOWLEDGEMENTS

Financial assistance of the University of Pretoria and the Foundation for Research Development is gratefully acknowledged.

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