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S. J. Archer^a; T. A. Modro^a; L. R. Nassimbeni^a

^a School of Chemical Sciences, University of Cape Town, Rondebosch, Republic of South Africa

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INTERACTIONS OF NUCLEOPHILES WITH QUATERNARY PHOSPHONIUM CENTERS Crystal and Molecular Structure of Benzyltriphenylphosphonium Iodide and Structural Correlation of Related Systems

S. J. ARCHER, T. A. MODRO and L. R. NASSIMBENI

*School of Chemical Sciences, University of Cape Town, Rondebosch 7700,
Republic of South Africa*

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The Crystal and molecular structure of benzyltriphenylphosphonium iodide was determined. This salt crystallises in space group $P2_1/c$, with $a = 9.692(5)$, $b = 21.58(1)$, $c = 11.211(6)\text{\AA}$; $\beta = 107.2(2)^\circ$; $Z = 4$. The structure was refined to a final R value of 0.052.

This structure, together with all structures of the quaternary phosphonium salts $R_4P^+ X^-$, available through the CCDC file, was subject to the correlation treatment, introduced by Dunitz *et al.* Exclusive "face" orientation of X^- with respect to the tetrahedral phosphonium center was demonstrated. Analysis of the secondary interactions of X^- with the organic cation indicated that systems studied yield better models for ylid formation (α -hydrogen abstraction) than models for nucleophilic attack at the P^{IV} atom.

Probing reaction paths by the Structure Correlation approach has introduced a fascinating tool for bridging the gap between chemical crystallography and reactivity. This approach involves the correlation of certain structural parameters for a series of related crystal structures, thus "mapping" a minimum energy pathway along the reaction coordinate; excellent reviews by Bürgi,¹ and Murray-Rust² are now available on this subject. When this method was applied to systems modelling such chemical processes as ligand exchange at a tetrahedral center (S_N2 mechanism),³ S_N1 -type dissociation,⁴ or nucleophilic addition to the carbonyl function,⁵ good agreement with the stereochemical characteristics accepted for these reactions was obtained.

The Structural Correlation method seems, for several reasons, particularly suitable for investigating systems consisting of nucleophiles interacting with the tetra-coordinated phosphorus atom. Firstly, ligand interchange at the phosphoryl group is at the core of the phosphorylation process. Secondly, nucleophilic substitution of the P^{IV} atom can follow a variety of mechanistic patterns, involving the decrease ("metaphosphate" mechanism), as well as the increase (tbp intermediate) of bonding at phosphorus, or the synchronous displacement of the leaving group by the nucleophilic reagent (S_N2-P mechanism). Each of these reaction types is characterized by different changes of molecular parameters (bond distances and angles, secondary bonds, etc.) at the phosphorus atom along the reaction coordinate. Finally, the stereochemical outcome of the substitution may be a function of the directional preferences of nucleophiles, and/or the polytopal rearrangements of the reaction intermediate.

In this work we want to report the preliminary results obtained for an ionic system $R_4P^+ X^-$ (I), i.e. the quaternary phosphonium salts. In general, a phosphonium ion can react with a nucleophile (or a base) in a variety of ways, the most important of which are:⁶ (i) nucleophilic attack at the positively charged phosphorus atom

(formation of the pentavalent intermediate), or (ii) abstraction of the α -proton from one of the substituents (ylid formation). The preference for a particular reaction depends upon various internal and external factors including the steric requirements for the approach of X^- to the phosphorus or α -carbon atom. For the reaction pathway (i) two distinct directions of approach are possible.⁷ In the so called "face" attack, the nucleophile meets less steric interference, but once the new bond is formed, group X is in a more congested (apical) position in the *tdp* product. The alternative "edge" approach, although sterically more hindered, results in a less crowded (equatorial) location of the incoming nucleophile. The apical ("face") entry is generally accepted on the basis of the stereochemistry of substitution, but no direct evidence for this type of spatial preference is available.

RESULTS AND DISCUSSION

The Cambridge Crystallographic Data Center (CCDC) file⁸ contains information of space group and positional atomic coordinates for all structures whose data have been published. A search of the CCDC file was carried out for structures corresponding to the formula (I). 25 such structures were found, from which the final set containing nine phosphonium salts has been selected. This set of compounds **1–9** comprises structures (I) having one group R which can be considered both as a potential leaving group in substitution reactions (carbanion precursor) and as a precursor of an ylid, via α -hydrogen abstraction (in seven structures R = benzyl, in one R is substituted allyl, and in another the β -ketoalkyl group). Since the crystal and molecular structure of benzyltriphenylphosphonium chloride (**1a**) was available,⁹ we decided to determine the structure of the corresponding iodide (**1b**) in order to evaluate the influence of the nucleophilicity (or basicity) of a counterion on the structural parameters of the phosphonium center. Figure 1 gives the plot of the phosphorus-anion X^- distances vs. four $C-P \cdots X$ angles for ten salts **1a**, **1b–9**.

The $P \cdots X$ distance Δd is given relative to the sum of the van der Waals radii,¹⁸ so $\Delta d = 0$ represents the distance corresponding to the sum of the vdw radii of atoms P and X. Figure 1 demonstrates the preferred orientation of ions X^- with respect to the tetrahedral phosphonium center. For the ideal "face" approach by a nucleophile, the $C-P \cdots X$ angles are 180° (one) and 70.5° (three); an ideal "edge" approach requires two $C-P \cdots X$ angles of 54.7° , and two of 125.3° . These directions are indicated on the diagram (by "F" and "E," respectively), and it is clear that with no exceptions the "face" approach is chosen. This directionality is retained even at a long range ($\Delta d > 1 \text{ \AA}$) indicating very long secondary interactions. In fact, the preference for the "face" orientation holds rigorously for all the (25) phosphonium salts included in the CCDC file.[†] This selectivity may be demonstrated clearly using the spherical polar representation of system (I). The phosphorus atom is placed at the origin, θ is the $C_1-P \cdots X$ angle, and ϕ is the angle $C_2-P \cdots X$, measured anticlockwise, projected onto the plane perpendicular to the vector C_1-P . Arbitrarily, C_1 is placed at the position at $\theta = 0$, and C_2 at the position corresponding to $\phi = 0$ (Figure 2).

[†] All structures studied correspond to the general formula (I), where R = Me, Et, Ph, Ph_3C , CH_2I , substituted alkyl, tetramethylene, substituted tetramethylene, etc; $X^- = Br^-$, I^- , BF_4^- , PF_6^- , $Hg(SCN)_3^-$.

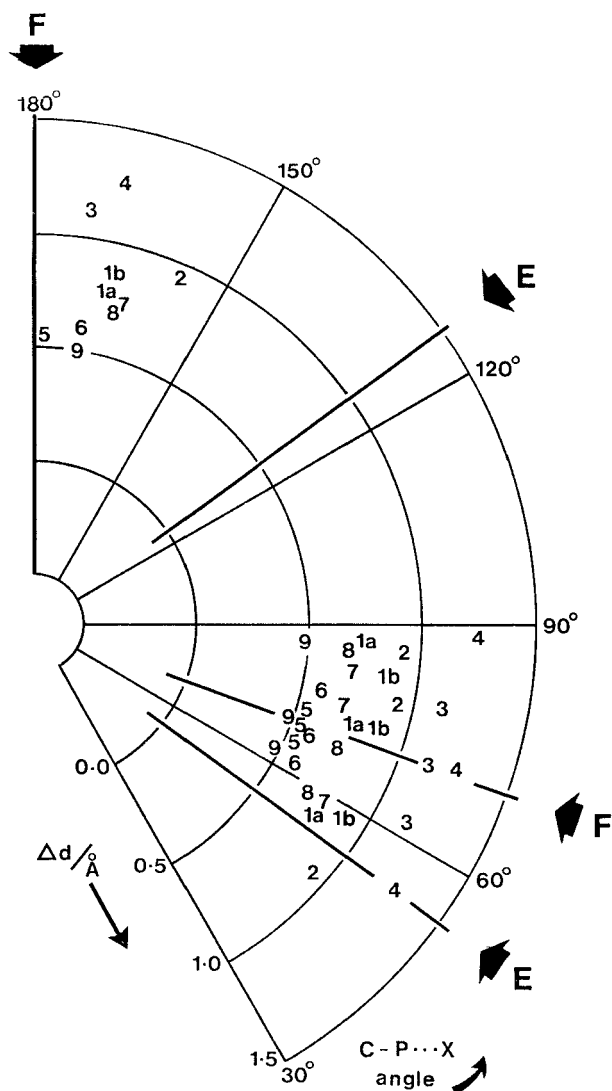
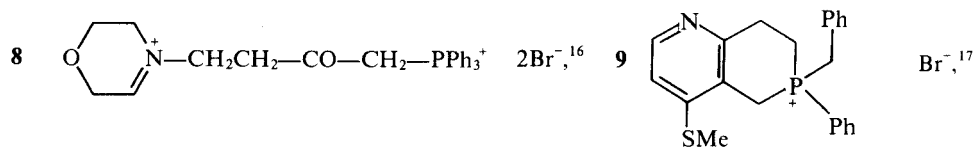


FIGURE 1 $\text{P} \cdots \text{X}$ distances vs $\text{C}-\text{P} \cdots \text{X}$ angles **1a**—Benzyltriphenylphosphonium chloride;⁹ **1b**—Benzyltriphenylphosphonium iodide (this work); **2**—Benzyl (2-methoxyphenyl)diphenylphosphonium bromide;¹⁰ **3**—Benzyltriphenylphosphonium iodosulfinate;¹¹ **4**—Benzyltriphenylphosphonium hexachlorouronate;¹² **5**—Benzylmethylphenylpropylphosphonium bromide;¹³ **6**—Benzylmethyl(1-naphthyl)phenylphosphonium bromide;¹⁴ **7**—(3,7-dimethyl-2,6-octadienyl)triphenylphosphonium bromide;¹⁵



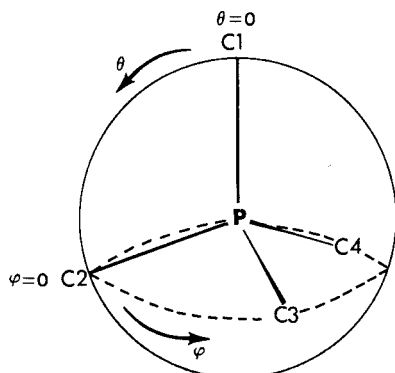


FIGURE 2 Spherical polar coordinate system.

The angular position of any nucleophile relative to phosphorus may be defined by two coordinates; θ the azimuthal angle and ϕ the equatorial angle. A Mercator Projection is a plot of θ vs ϕ ; such a projection of the all available structures (I) is presented in Figure 3.

The directions of the carbon atoms C_2 , C_3 , C_4 appear as close groupings around the points $\theta = 110.7^\circ$, $\phi = 0^\circ$, 120° , 240° (tetrahedral structure), and points representing $P \cdots X$ directions are distributed more loosely around the values of $\theta = 60^\circ$, and $\phi = 60^\circ$, 180° , 300° . By considering the absence of points in the regions of $\theta = 125.3^\circ$, $\phi = 60^\circ$, 180° , 300° , and $\theta = 54.7^\circ$, $\phi = 120^\circ$, 240° , 360° , it is clear that the "face" approach is exclusively adopted by nucleophiles.

In salts **1-9** the distances between the nucleophiles and the phosphorus atom are still rather large ($0.5 \text{ \AA} \leq \Delta d \leq 1.25 \text{ \AA}$) (see Figure 1). In addition, for all the cations **1-9** we observed no significant departure of the $C-P-C$ angles from the tetrahedral angle. Thus, if the structures studied are to be considered as models for the substitution reaction, they represent "early" points on the reaction coordinate. A recent study¹⁹ on sulfonium salts demonstrated similar directional preferences, but at the same time much shorter contacts between anions and sulfur atom ($-0.3 \text{ \AA} < \Delta d < +0.4 \text{ \AA}$). The probable reason for this difference is that sulfonium centers are sterically less hindered (only three ligands in the tetrahedral environment of sulfur) and thus more susceptible to the nucleophilic approach. Structures **1-9** are however poor models for the nucleophilic substitution reaction at phosphorus for another, more important reason. Although in all systems **1-9** the nucleophile has a "face" approach, (within $\pm 20^\circ$ of linearity), in no case does this approach occur opposite the potential leaving group (benzyl, allyl or ketoalkyl). The anions X^- are invariably located opposite an aromatic substituent, and this aversion of X^- to aromatic groups can be easily seen by analyzing the deviations of the smaller $C-P \cdots X$ angles from the pure "face" value at 70.5° . In each case the nucleophile tends to "lean" away from the remaining aromatic substituent(s). For example, in **6**, where the bromide ion is located in the vicinity of the Me, Ph and CH_2Ph groups (opposite to the naphthyl substituent), the angle $C(Ph)-P \cdots Br$ is 76.9° , while angles $C(Me)-P \cdots Br$ and $C(CH_2Ph)-P \cdots Br$ are 61.6° and 68.4° , respectively. Similarly, in **1a**, angles $C(Ph)-P \cdots Cl$ are considerably greater than the angle $C(CH_2Ph)-P \cdots Cl$. On the other hand, for structure **5**, where the bromide ion once located opposite to the phenyl group interacts only with the saturated α -carbon atoms (benzyl, methyl and propyl), the theoretical values of all $C-P \cdots Br$

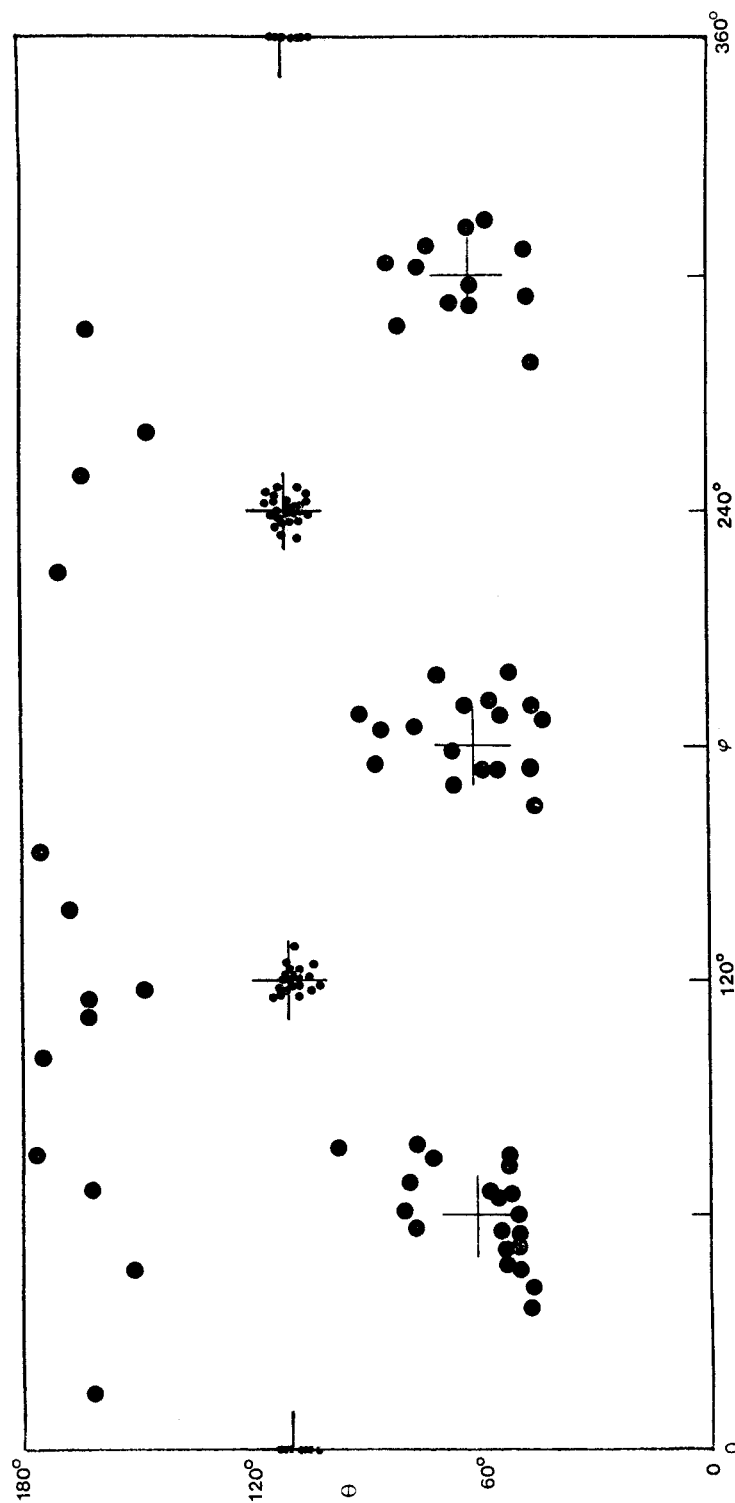
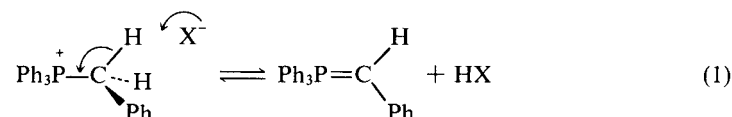


FIGURE 3 Mercator projection of the quaternary phosphonium salts (I). Small circles represent $\text{P}-\text{C}$ directions; large circles represent $\text{P} \cdots \text{X}$ directions, and crosses show the theoretical points for the tetrahedral arrangement ($\text{P}-\text{C}$ directions) and "face" approach ($\text{P} \cdots \text{X}$ directions).

angles which are expected for an ideal "face" approach, are observed. The apparent tendency of nucleophiles to avoid aromatic groups is probably due to repulsion between the negative charge of the nucleophiles and the Π electrons of the aromatic systems.

Comparison of benzyltriphenylphosphonium chloride (**1a**) and iodide (**1b**) shows that there is no significant difference in the closest $P \cdots X$ distances. $\Delta d(P \cdots X)$ values for **1a** and **1b** are +0.75 and +0.86 Å; considered as fractions of the corresponding sum of the van der Waals radii they are very close to each other. It seems that the greater nucleophilicity of the iodide (relative to the chloride) ion is counterbalanced by its greater bulk inhibiting closer approach in the sterically congested environment of the phosphorus atom. The effect of the steric bulk and charge dispersion of the anion X^- can be demonstrated by comparing the $P \cdots X$ distances in four benzyltriphenylphosphonium salts, **1a**, **1b**, **3**, and **4**. In both **1a** (chloride) and **4** (hexachlorouranate) the measured values refer to the $P \cdots Cl$ distance; however, due to the great size and considerable charge delocalization of the UCl_6^- anion, this distance is much longer (4.80 Å) in **4** than in **1a** (4.30 Å). Similarly, the $P \cdots I$ distance in **1b** is 4.64 Å, but in the iodosulfinate salt **3** this distance is increased to the value of 4.94 Å. A perspective view of **1b** is presented in Figure 4.

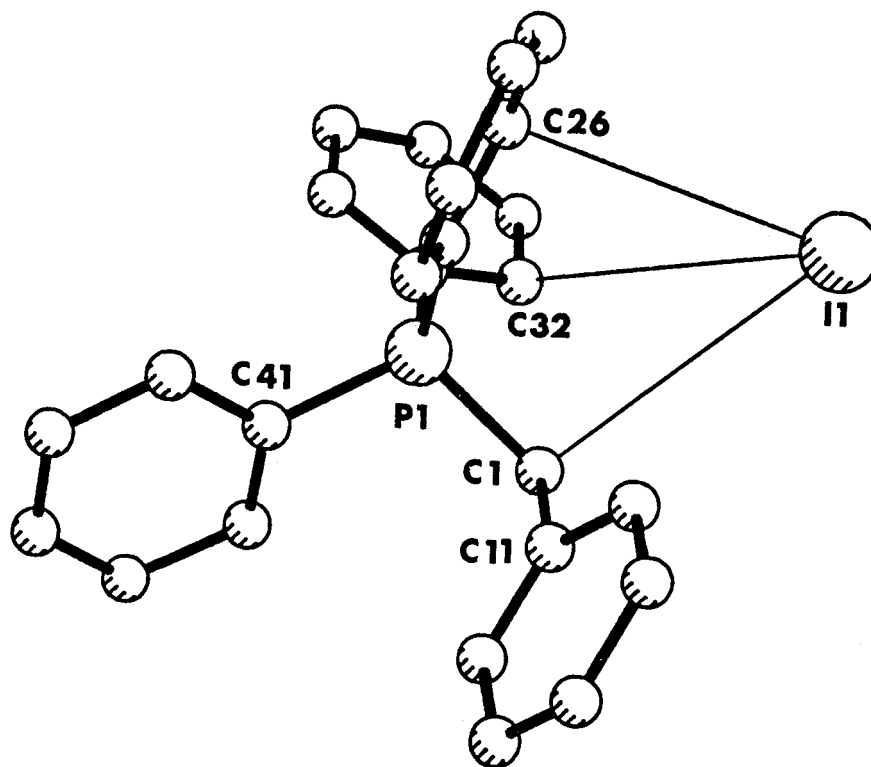
We note that the iodide ion in **1b** does not lie opposite the potential leaving group (benzyl), but on the contrary, exhibits the shortest secondary contact $C \cdots I$ with the benzylic carbon atom C_1 . The shortest contacts $C \cdots I$ in **1b** are: $C_1 \cdots I = 3.96$ Å; $C_{26} \cdots I = 4.00$ Å; $C_{32} \cdots I = 4.18$ Å ($d_{vdw} = 3.68$ Å). This result indicates the possibility of some interactions between ion X^- and the acidic α -hydrogen atoms. Thus the system might be considered as a model for ylid formation from a phosphonium ion and a base:



Reaction (1) should result in a change of the $P-C_\alpha-C(\text{Ph})$ angle from the tetrahedral to the planar trigonal value. The bond angles at the ylid carbon correspond to the value expected for the sp^2 carbon; e.g. the $H-C-H$ angle in $\text{Ph}_3\text{P}=\text{CH}_2$ is 124.2° ,²⁰ and the $Cl-C-C(0)$ angle in $\text{Ph}_3\text{P}=\text{C}(\text{Cl})\text{COPh}$ is 121.2° .²¹ It is interesting to note that in both ions **1**, the $P-C_\alpha-C(\text{Ph})$ angle is significantly greater than the tetrahedral angle; the corresponding values are 114.7° for **1a**, and 113.2° for **1b**.

We have analyzed all the secondary $C_1 \cdots X$ bonds in structures **1-9** and found in all cases some indications of weak interactions between X^- and α -carbons, precursors of the carbanionic centers. This trend seems to be more pronounced than the secondary interactions between X^- and the P atom; the relevant data are presented in Table I.

With exceptions of structures **3**, **4** and **9**, $C_1 \cdots X$ distances are only slightly greater than the corresponding sum of Van der Waals radii. For salts, **1a**, **1b**, **2**, and **5-8**, the average Δd , relative to the d_{vdw} value, is +5.9%. Compounds **3** and **4** contain highly delocalized anions for which no significant directional interactions with the organic cation are expected. It can however be pointed out that in **3** the iodosulfinate anion behaves as a precursor of I^- and SO_2 ; the $P \cdots I$ secondary bond is shorter than the remaining oxygen-phosphorus secondary bonds. In **9** the phosphorus atom is incorporated in the ring, and some possible directions of nucleophilic approach are excluded.

FIGURE 4 Perspective view of benzyltriphenylphosphonium iodide (**1b**).TABLE I
 $\text{X}^- \dots \text{C}_i^a$ and $\text{X}^- \dots \text{P}^+$ secondary bonds in salts **1**–**9**.

Structure and CCDC acronym	$\text{C}_i \dots \text{X}^-$ Å	d_{vdw} Å	Δd Å	Δd %	$\text{P}^+ \dots \text{X}^-$ Å	d_{vdw} Å	Δd Å	Δd %
1a BZPPPOS	3.56	3.45	0.11	3.2	4.30	3.55	0.75	21.1
1b —	3.96	3.68	0.28	7.6	4.64	3.78	0.86	22.8
2 BMPPHB	3.64	3.55	0.09	2.5	4.59	3.65	0.94	25.7
3 BZTPPI	4.39	3.68	0.71	19.3	4.94	3.78	1.16	30.7
4 TPBZPU	4.00	3.45	0.55	15.9	4.80	3.55	1.25	35.2
5 MPBPBR	3.92	3.55	0.37	10.4	4.22	3.65	0.57	15.6
6 BZMNPB	3.96	3.55	0.41	11.5	4.25	3.65	0.60	16.4
7 MOCTPB	3.66	3.55	0.11	3.1	4.44	3.65	0.79	21.6
8 OMBPPB	3.66	3.55	0.11	3.1	4.36	3.65	0.71	19.4
9 HTPOPY	4.50	3.55	0.95	26.8	4.15	3.65	0.50	13.7

^a For **1**–**6**, and **9** C_i represents benzylic CH_2 group; for **7** C_i is substituted allylic CH_2 group; for **8** C_i is the CH_2 group of the $\text{CH}_2\text{—CO—R}$ substituent.

We note that the average value of $\Delta d(C_i \dots X)$ equals ca. + 6% of the vdw distance and refers to a system in which two α -hydrogen atoms are present at C_i , and these certainly occupy some space. We believe therefore that the observed proximity of anions X^- and methylene carbons C_i is of a general nature and results from the weak hydrogen bonding of the type $P^+-C-H \dots X^-$, analogous to that postulated for the quaternary ammonium salts from IR spectrophotometric data.²²

Secondary bonds between ions X^- and the positively charged phosphorus seem to be weaker than those with respect to the α -CH moiety. From Table I it follows that (after excluding salts 3 and 4, with the delocalized anions), the average value of $\Delta d(P \dots X)$, expressed as a percentage of the d_{vdw} value, is +17.8%, i.e. three times greater than the corresponding value for the $C_i \dots X$ distance.

We recognize that this difference is not necessarily the straightforward consequence of the strength of the corresponding secondary interactions. The "face" approach of X^- to the phosphorus is hindered by three α -carbon atoms and the larger (relative) values of the $\Delta d(P \dots X)$ distance can be, at least partly, a result of simple steric interactions. Nevertheless, we conclude that the simple phosphonium salts like 1-9 correspond better to the early stage of the ylid formation than to the apical entry of the nucleophile to the tetrahedral phosphonium system to form the trigonal bipyramidal structure.

We are convinced that the detailed analysis of crystal and molecular structures offers a fresh insight into the dynamics of the organophosphorus compounds. Two approaches in such studies are possible. One involves using the molecular parameters as a basis for theoretical calculations of the chemical behavior, and comparing

TABLE II
Crystal data and experimental and refinement parameters for the crystal structure of
benzyltriphenylphosphonium iodide

Crystal data	
Molecular formula	$(C_6H_5CH_2)(C_6H_5)_3P^+I^-$
M_r	480.32
Space group	$P2_1/c$
a	9.692(5) Å
b	21.58(1) Å
c	11.211(6) Å
β	107.2(2)°
V	2239.67 Å ³
D_m	1.41 Mg m ⁻³
D_c	1.42 Mg m ⁻³ for $Z = 4$
μ (MoK α)	1.39 mm ⁻¹
$F(000)$	960
Data collection	
Crystal dimensions	0.32 × 0.24 × 0.16 mm
Scan mode	$\omega - 2\theta$
Scan width	1.0° θ
Scan speed	0.03° θ s ⁻¹
Range scanned (2θ)	6-46°
Stability	2%
Number of reflections collected	3206
Number of observed reflections	$I(\text{rel}) > 3\sigma I(\text{rel})$
Number of variables	120
$R = \sum F_o - F_c / \sum F_o $	0.052
$R_w = \sum w^{1/2} F_o - F_c / \sum w^{1/2} F_o $	0.056
Weighting scheme w	$(\sigma^2 F + 0.00062 F^2)^{-1}$
U of constrained H atoms	0.112 Å ²

the results with experimental data. Such an approach was successfully applied by Holmes and coworkers,²³ to the base-catalyzed hydrolysis of cyclic phosphonium salts. The second approach based on the Structural Correlation method, requires structural analysis of suitably selected models in order to evaluate spatial characteristics of the chemical process taking place in the vicinity of the phosphorus atom. Such investigation is now being carried out in this laboratory.

EXPERIMENTAL

Preparation of 1b

A saturated aqueous solution of **1a** (Merck) was added to a saturated aqueous solution of sodium iodide. An immediate dense white precipitate was obtained. The product was filtered, washed with water and dried. Anal. Calc. for $\text{C}_{25}\text{H}_{22}\text{IP}$: C, 62.5; H, 4.6. Found: C, 62.2; H, 4.5. For the X-ray analysis the sample was prepared by slow evaporation of an ethanolic solution of **1b**. Small, hexagonal prisms were obtained. The lattice constants were obtained by a least squares method from the setting of 25 reflections measured on a four-circle diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.7107\text{\AA}$). During data collection, three reference reflections were periodically monitored to check crystal stability. Crystal data and experimental details are listed in Table II. The data were corrected for Lorentz polarization, but not for absorption.

TABLE III

Fractional atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$). ESD/S are in parenthesis

	X	Y	Z	U11	U22	U33	U23	U13	U12
I(1)	2087(1)	571(1)	2702(1)	49(0)	62(0)	62(0)	9(0)	8(0)	2(0)
P(1)	5883(2)	1387(1)	6448(2)	39(1)	44(1)	46(1)	3(1)	17(1)	5(1)
C(1)	4832(7)	681(2)	6051(6)	43(1)					
C(11)	3811(7)	582(3)	6823(6)	46(1)					
C(12)	2448(8)	804(3)	6440(7)	65(2)					
C(13)	1450(10)	684(4)	7132(8)	80(2)					
C(14)	1923(9)	371(4)	8220(8)	73(2)					
C(15)	3312(8)	152(4)	8638(7)	68(2)					
C(16)	4273(8)	247(3)	7931(6)	55(1)					
C(21)	6865(6)	1369(3)	8065(5)	43(1)					
C(22)	6182(7)	1472(3)	8991(6)	53(1)					
C(23)	6939(8)	1395(3)	10232(7)	60(2)					
C(24)	8356(8)	1226(3)	10576(7)	62(2)					
C(25)	9044(8)	1116(3)	9689(7)	62(2)					
C(26)	8325(7)	1195(3)	8444(6)	53(1)					
C(31)	7131(6)	1432(3)	5544(5)	43(1)					
C(32)	7394(8)	938(3)	4868(7)	64(2)					
C(33)	8392(10)	996(4)	4191(8)	80(2)					
C(34)	9106(8)	1540(3)	4199(7)	65(2)					
C(35)	8868(9)	2033(4)	4864(7)	76(2)					
C(36)	7862(8)	1975(4)	5561(7)	68(2)					
C(41)	4719(7)	2053(3)	6084(6)	48(1)					
C(42)	4912(8)	2558(3)	6875(7)	64(2)					
C(43)	4048(10)	3076(4)	6516(9)	89(2)					
C(44)	3048(10)	3080(5)	5411(9)	93(3)					
C(45)	2828(10)	2610(4)	4566(9)	89(2)					
C(46)	3703(8)	2066(4)	4924(7)	67(2)					

TABLE IV
Principal bond lengths (Å) and angles (degrees)

C(1)	—P(1)		1.812(5)
C(21)	—P(1)		1.782(6)
C(31)	—P(1)		1.796(6)
C(41)	—P(1)		1.799(6)
C(11)	—C(1)		1.510(10)
C(21)	—P(1)	—C(1)	108.9(3)
C(31)	—P(1)	—C(1)	109.4(3)
C(41)	—P(1)	—C(1)	110.3(3)
C(31)	—P(1)	—C(21)	109.2(3)
C(41)	—P(1)	—C(21)	110.9(3)
C(41)	—P(1)	—C(31)	108.0(3)
C(11)	—C(1)	—P(1)	113.2(5)

Solution for refinement of the structure

1b was solved by locating the I atom in a Patterson map; subsequent weighted difference syntheses yielded the positions of all remaining non-hydrogen atoms. After further refinement with I and P atoms treated anisotropically, most of the H atoms appeared in a difference map. These were included in the final model, and were constrained at 1.08 Å from their corresponding C atoms, their positions being dictated by the geometry of the molecule. Details of the final refinement are given in Table II. Table III shows the final atomic coordinates and temperature factors, and a selection of bond lengths and angles appear in Table IV.

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