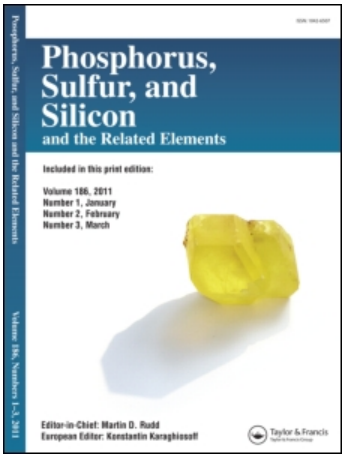

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE CRYSTAL AND MOLECULAR STRUCTURE OF BENZYL (2-METHOXYPHENYL)-DIPHENYLPHOSPHONIUM BROMIDE

John S. Wood[a]; Ronald J. Wikholm[a]; William E. McEwen[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, MA.

To cite this Article Wood, John S. , Wikholm, Ronald J. and McEwen, William E.(1977) 'THE CRYSTAL AND MOLECULAR STRUCTURE OF BENZYL (2-METHOXYPHENYL)-DIPHENYLPHOSPHONIUM BROMIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 3: 2, 163 — 169
To link to this Article: DOI: 10.1080/03086647708077706
URL: http://dx.doi.org/10.1080/03086647708077706

Phosphorus and Sulfur
1977, Vol. 3, pp. 163–169

THE CRYSTAL AND MOLECULAR STRUCTURE OF BENZYL(2-METHOXYPHENYL)-DIPHENYLPHOSPHONIUM BROMIDE

JOHN S. WOOD, RONALD J. WIKHOLM, and WILLIAM E. McEWEN

Contribution from the Department of Chemistry of
The University of Massachusetts, Amherst, MA. 01002

(*Received December 16, 1976*)

The crystal structure of benzyl(2-methoxyphenyl)diphenylphosphonium bromide has been determined from three dimensional X-ray data collected on a three circle diffractometer using MoKα radiation. The salt crystallized in the orthorhombic space group *Pbca* with cell constants a = 15.528 (7), b = 16.892 (7), and c = 17.921 (8) A. The observed and calculated densities for 8 molecules per unit cell are 1.308 (5) and 1.309 g · cm^{-3} respectively. The structure was refined by full matrix least squares to final residuals of R = 0.089 and R_w0.120 for the 1757 independent reflections in the range $2^\circ > 2\theta > 42^\circ$ whose intensities were above background. The cation has near tetrahedral geometry with an average P–C bond distance of 1.819 (14) A and the configuration of the ion is such that the oxygen atom of the methoxy group is trans to the alkyl carbon atom of the benzyl group. The phosphorus-oxygen distance of 2.878 (12) A suggests a weak bonding interaction and qualitative support for this view is obtained from energy minimization calculations in which the total steric energy made up primarily of bond stretching energies and van der Waals non-bonded interactions is treated. The results are in accord with nmr data previously reported and from which it was concluded that a weak bonding interaction between the methoxy oxygen and the phosphorus atoms causes an upfield shift of the methyl protons of the benzyl group. The molecular structure of the phosphonium cation depicted herein makes it highly improbable that the observed chemical shift is attributable to a magnetic anisotropic effect.

Rate data for the quaternization reactions of various triarylphosphines with benzyl chloride, benzyl bromide, and *n*-butyl chloride, and of aryldiethylphosphines with ethyl iodide have been presented in previous papers.[1-3] Three particularly striking effects were noted. (1) The presence of an *o*-methoxy substituent in an aryl group of the phosphine causes a significant acceleration of the reaction. (2) The ratio of the rates of reaction of a given triarylphosphine with benzyl chloride and *n*-butyl chloride is less than 20, probably the smallest such ratio ever found in S_N2 reactions of these halides. (3) Rate and activation parameter profiles are distinctly different for anisyldialkylphosphines and anisyldialkylamines in reactions with alkyl halides. An explanation of these effects was suggested, based partly on the concept of overlap of a pair of 2*p* electrons of a 2-methoxyphenyl group with a 3*d* orbital (or hybrid orbital) of phosphorus in the transition state,[4] and partly on the concept that the transition state for each of these reactions lies much closer to the reagents than to the products along the reaction coordinate of the energy profile diagram. It has also been pointed out[1-3] that, if such an effect exists in the transition state of the S_N2 reaction, it will also be apparent to an even larger degree in the phosphonium cation which is the product of the reaction. For reasons cited in the previous papers,[1-3] the chemical shift of the protons of the methylene group directly bonded to phosphorus in the phosphonium salt represents the best probe of the presumed overlap effect in the nmr spectrum of each compound. An upfield shift of the methylene hydrogens is expected when the electron density at phosphorus is increased owing to an overlap effect. A previous caveat that the effect may instead be attributable to a magnetic anisotropic influence of one of the substituent groups can now be dispensed with on the basis of the structural data being presented herin. To provide additional information about the presumed overlap effect, the crystal structure of benzyl(2-methoxyphenyl)diphenylphosphonium bromide has now been determined from three dimensional X-ray data collected on a three circle diffractometer using MoKα radiation.

The configuration of the phosphonium ion is illustrated in Figure 1, and the pertinent structural information is given in Tables I and II. The average P–C distance is 1.819 (14), and no individual value differs significantly from this value although the P–CBZ distance, involving an sp^3 carbon might be

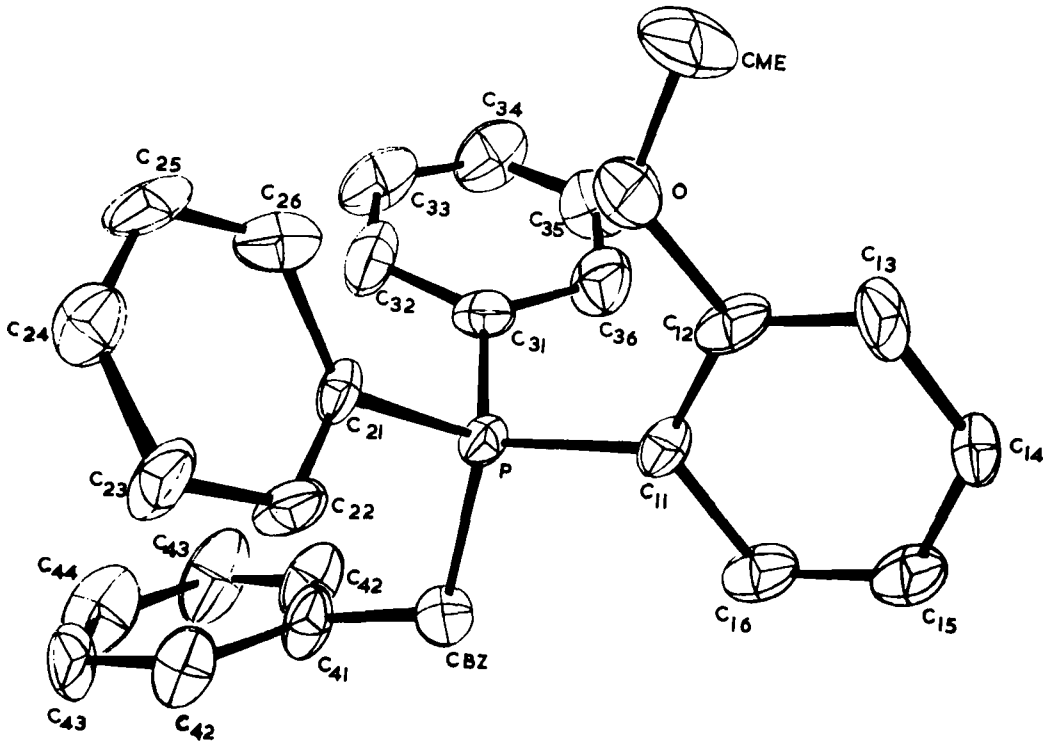

FIGURE 1. A perspective view of the benzyl(2-methoxyphenyl)diphenylphosphonium ion. The thermal ellipsoids are drawn at the 33% probability level.

expected to be *ca.* 0.03 Å longer than the other P–C distances. Similarly, the bond angles at phosphorus do not differ significantly from the average (tetrahedral) value of 109.45 (1.02)° so that, although three different ligands with differing steric requirements are bonded to phosphorus, they do not produce any significant deviation from the idealized T_d geometry for the coordination sphere. It thus appears that these differing steric forces are minimized by the relative conformations of the phenyl rings and this point is supported by the energy minimization calculations. The bond distances observed here are in accord with phosphorus-carbon distances reported for other structures containing four coordinate phosphorus. Thus in $[(C_6H_5)_4P]I$, the P–C distance is 1.80 Å[6] while in $[(C_6H_5)_3(C_2H_5)P]_2[Ce(NO_3)_5]$ the $P–C_{(Et)}$ distance is 1.886 (25) Å and the three $P–C_\phi$ distances average 1.795 (26) Å. In the uncharged molecules $(C_6H_5)_3PCCX$ (X = O and S) the $P–C_\phi$ distances average 1.805 (6)[8] and 1.795 (7)[9] respectively. To within the estimated standard deviations, the four ligands appear to be planar (Table II) and the phosphorus atom is displaced from the best planes of groups I, II, and III by only 0.055 (9), 0.057 (8), and 0.089 (8) Å respectively.

As noted previously, the principal reason for undertaking the structure analysis was to obtain a value for the phosphorus-oxygen distance, in the hope that this would give a qualitative indication of the magnitude of the P–O interaction. The observed distance of 2.878 (14) Å is appreciably less than the sum of the generally accepted van der Waals radii,[10] namely 3.30 Å and is also less than the P–O distance (3.05 Å) reported in 2-troponylethoxycarbonylmethylenetriphenylphosphonium betaine[11] and which is believed to be indicative of such an interaction. Interactions of a similar kind have also been reported in two triphenylarsonium acetylcyclopentadienides,[12,13] where in one of these compounds an especially short $As^+ \ldots O^-$ interaction of 2.770 (3) Å has been observed. In addition, examination of bond angle data supports the presence of a weak P–O interaction. The angle O–C(12)–C(11) at 111.3° is considerably decreased from its ideal value of 120°, while there is a corresponding increase in O–C(12)–C(13), so that the net result is a decrease in the P–O distance from that expected, assuming sp^2 angles at carbon.

The pertinent results of the steric energy minimization calculations, in the form of bond distances and angles are summarized in Table III, and these provide

TABLE I

Bond distances (Å) and angles (deg.) in $P(C_6H_5)_2(CH_2C_6H_4)(C_6H_4OCH_3)^+Br^-$ (standard deviations in parentheses)

P–C(11)	1.799 (13)	P–C(31)	1.824 (14)
P–C(21)	1.838 (14)	P–CBZ	1.814 (14)
	P–O′ 2.878 (12)		
C(11)–P–C(21)	109.6 (6)	C(21)–P–C(31)	111.9 (7)
C(11)–P–C(31)	110.0 (7)	C(21)–P–C(BZ)	109.0 (6)
C(11)–P–CBZ	108.3 (6)	C(31)–P–C(BZ)	107.9 (7)
	P–CBZ–C(41) 114.7 (9)		
C(11)–C(12)	1.403 (22)	C(11)–C(16)	1.414 (21)
C(12)–C(13)	1.366 (23)	C(13)–C(14)	1.383 (24)
C(14)–C(15)	1.373 (24)	C(15)–C(16)	1.387 (22)
C(11)–C(12)–C(13)	123.2 (14)	C(12)–C(13)–C(14)	119.8 (15)
C(13)–C(14)–C(15)	120.1 (15)	C(14)–C(15)–C(16)	119.3 (14)
C(15)–C(16)–C(11)	122.8 (14)	C(16)–C(11)–C(12)	119.7 (13)
O–C(12)	1.401 (20)	O–CME	1.446 (27)
C(11)–C(12)–O	111.3 (13)	C(13)–C(12)–O	123.2 (15)
C(12)–O–CME	117.0 (15)	O–P–CBZ	161.1 (5)
C(21)–C(22)	1.351 (21)	C(22)–C(23)	1.401 (23)
C(23)–C(24)	1.364 (26)	C(24)–C(25)	1.349 (27)
C(25)–C(26)	1.410 (27)	C(26)–C(21)	1.392 (24)
C(21)–C(22)–C(23)	120.5 (15)	C(22)–C(23)–C(24)	119.1 (16)
C(23)–C(24)–C(25)	122.5 (17)	C(24)–C(25)–C(26)	119.9 (17)
C(25)–C(26)–C(21)	117.6 (17)	C(26)–C(21)–C(23)	121.4 (15)
C(31)–C(32)	1.418 (23)	C(32)–C(33)	1.344 (27)
C(33)–C(34)	1.327 (35)	C(34)–C(35)	1.296 (30)
C(35)–C(36)	1.387 (25)	C(36)–C(31)	1.366 (24)
C(31)–C(32)–C(33)	124.4 (17)	C(32)–C(33)–C(34)	118.8 (20)
C(33)–C(34)–C(35)	120.9 (20)	C(34)–C(35)–C(36)	121.9 (19)
C(35)–C(36)–C(31)	121.3 (16)	C(36)–C(31)–C(32)	112.6 (15)
CBZ–C(41)	1.548 (18)	C(41)–C(42)	1.368 (22)
C(42)–C(43)	1.504 (28)	C(43)–C(44)	1.326 (32)
C(44)–C(45)	1.314 (38)	C(45)–C(46)	1.311 (26)
C(46)–C(41)	1.354 (19)		
CBZ–C(41)–C(42)	120.5 (13)	CBZ–C(41)–C(46)	121.1 (12)
C(41)–C(42)–C(43)	114.0 (16)	C(42)–C(43)–C(44)	119.2 (20)
C(43)–C(44)–C(45)	129.1 (23)	C(44)–C(45)–C(46)	114.9 (20)
C(45)–C(46)–C(41)	129.3 (17)	C(46)–C(41)–C(42)	119.4 (14)

TABLE II

Least squares plane data for the $P(C_6H_5)_2(CH_2C_6H_5)(C_6H_4OCH_3)^+$ Ion[a]

Plane 1	$0.3271X - 0.7836Y + 0.5282Z = -1.509$							
Atom	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)	O	CME
Distance	−0.023	−0.023	−0.044	0.016	0.036	0.001	0.027	−0.014
Plane 2	$0.4083X + 0.7494Y + 0.5213Z = 11.810$							
Atom	C(21)	C(22)	C(23)	C(24)	C(25)	C(26)		
Distance	−0.011	0.0	0.015	−0.023	0.005	0.014		
Plane 3	$-0.8488X - 0.5197Y + 0.0972Z = -6.461$							
Atom	C(31)	C(32)	C(33)	C(34)	C(35)	C(36)		
Distance	−0.013	0.017	−0.004	−0.014	0.008	0.007		
Plane 4	$-0.9577X - 0.0627Y + 0.2810Z = 0.259$							
Atom	C(41)	C(42)	C(43)	C(44)	C(45)	C(46)	CBZ	
Distance	0.007	0.010	0.002	−0.015	−0.013	0.019	−0.009	

[a] The form of the least squares plane is $lX + mY + nZ = d$ where X, Y, and Z are orthogonal coordinates in Å. The weights used were for the ith atom $w_i = (a\sigma_x b\sigma_y c\sigma_z)^{-2/3}$.

TABLE III

Summary of results of energy minimization calculations—selected distances and angles

(a) Excluding P–O interaction:				
P–C(11)	1.852	C(11)–P–C(21)	106.6°
P–C(21)	1.850	C(11)–P–C(31)	110.4°
P–C(31)	1.851	C(11)–P–CBZ	111.2°
P–CBZ	1.854	C(21)–P–C(31)	112.9°
P–O	3.074	C(21)–P–CBZ	110.2°
		C(31)–P–CBZ	105.5°
O–P–C(11)	52.0°	C(11)–C(12)–O	119.7°
		C(13)–C(12)–O	119.8°
(b) Including P–O interaction:			
P–C(11)	1.846	C(11)–P–C(21)	106.8°
P–C(21)	1.850	C(11)–P–C(31)	110.8°
P–C(31)	1.851	C(11)–P–CBZ	110.4°
P–CBZ	1.854	C(21)–P–C(31)	113.0°
P–O	2.903	C(21)–P–CBZ	110.1°
		C(31)–P–CBZ	105.7°
O–P–C(11)	55.0°	C(11)–C(12)–O	116.3°
		C(13)–C(12)–O	123.1°

further support for the conclusions drawn from the structural data. The inclusion of the phosphorus-oxygen interaction m.dyn $Å^{-1}$, leads to a small but significant decrease in the P–O distance and along with this decrease there is a concomitant change in the two bond angles O–C(12)–C(11) and O–C(12)–C(13) away from near equality, toward the values obtained from the structure analysis. There is little change in the remaining dimensions of the phosphorus coordination geometry when compared to those obtained neglecting the P–O interaction.

Examination of the structure of benzyl(2-methoxyphenyl)diphenylphosphonium bromide (Figure 1) and of a Fisher-Hirschfelder-Taylor model of the compound shows that there is no reasonable way in which the 2-methoxyphenyl or the other phenyl groups could cause an upfield shift of the methylene protons through magnetic anisotropy.[14] Thus, the previously reported[1-3] upfield shift of the methylene protons of benzyl(2-methoxyphenyl)diphenylphosphonium

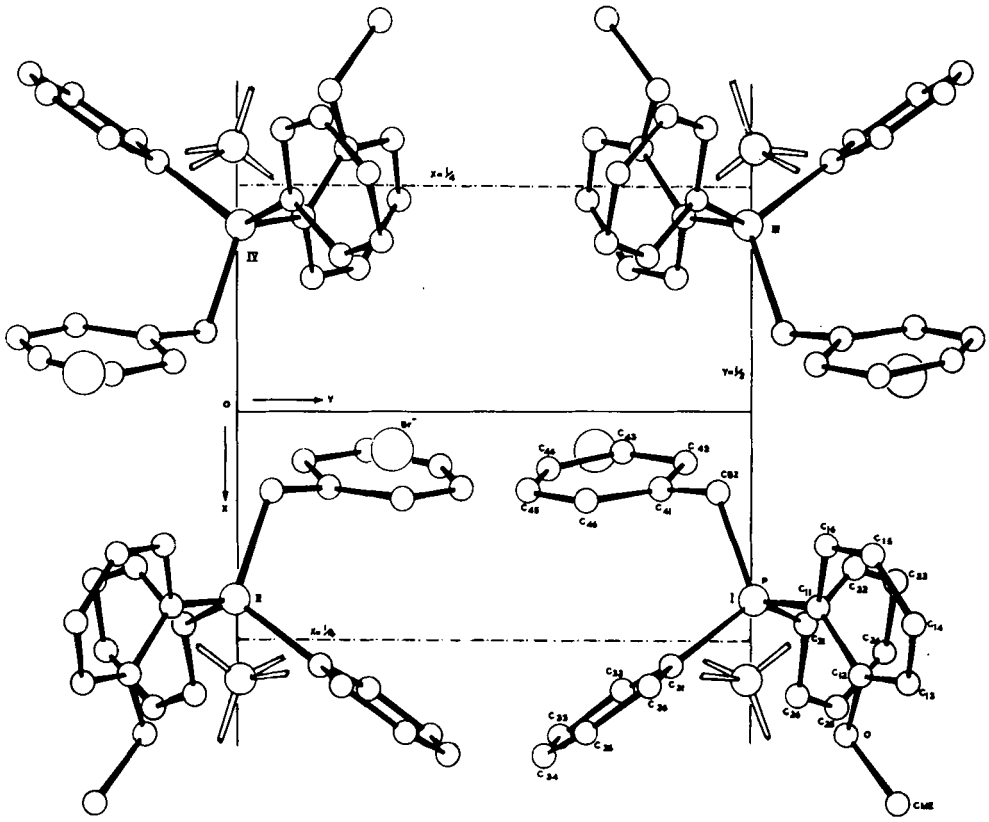

FIGURE 2. An [001] projection of a portion of the unit cell of $P(C_6H_5)_2(CH_2C_6H_5)(C_6H_4OCH_3)Br$. The numbered atoms define the asymmetric unit (Table V), and the molecules illustrated, are for positions x, y, z (I); $x, \frac{1}{2} - y, \frac{1}{2} + z$ (II); $-x, -y, -z$ (III) and $-x, \frac{1}{2} + y, \frac{1}{2} - z$ (IV) in *Pbca*.

bromide as against those of benzyltriphenylphosphonium bromide can now be accepted as additional evidence of a weak bonding interaction between oxygen and phosphorus in the former compound.

A projection of a portion of the structure of one unit cell, showing the packing of the phosphonium and bromide ions viewed down the crystal z axis, is illustrated in Figure 2.

EXPERIMENTAL SECTION

Preparation of benzyl(2-methoxyphenyl)diphenylphosphonium bromide. The preparation and properties of this compound have been described elsewhere.[2]

Collection of x-ray diffraction data. The crystal used for the diffraction study was an irregular shaped platelet with only forms {001} well developed. It was mounted along its extended [110] direction and had dimensions 0.48 mm x 0.40 mm x 0.23 mm. Preliminary photographic studies using precession techniques and AgKα radiation yielded approximate unit cell dimensions, showed D_{2h} (mmm) Laue symmetry, and indicated systematic absences, $h0l$ for $l = 2n + 1$, $0kl$ for $k = 2n + 1$ and $hk0$ for $h = 2n + 1$. These extinctions indicate the centrosymmetric orthorhombic space group *Pbca* [No. 61].

The crystal was transferred to an Enraf-Nonius CAD-3 diffractometer and aligned with the [110] diffraction vector parallel to the ϕ axis. Unit cell dimensions were obtained by least squares refinement of the accurate setting angles of 18 high angle reflections centered using the program SETANG.[15] As a check on absorption, the intensity of the strong 220 and 440 reflections were measured at $\chi = 90°$ and at intervals in ϕ of 15°. The resulting variation in intensity [(max.-min.)/average] amounted to *ca.* 6.5%. Since the maximum variation in specimen dimension occurred in the 110 plane, it was felt that the ϕ scans indicated the probable range of crystal transmission factors, giving a maximum correction of F of *ca.* 6%. As the crystal faces could not be unambiguously indexed and the ϕ scans showed a relatively small variation absorption corrections were not made.[16] Details of the data collection, crystal parameters, etc. are provided in Table IV.

Solution and refinement of the structure. Computations were carried out initially on a CDC-3800 computer and later, on a CDC-6600, using local modifications of Zalkin's FORDAP Fourier program, Prewitt's SFLS5 full-matrix least squares routine and various locally written programs. Scattering factors for Br^-, neutral phosphorus, carbon, and oxygen were taken from the compilation of Cromer and Waber[17] while for hydrogen, the scattering factor of Stewart *et al.*[18] was used. The function minimized in the least squares refinement was $\Sigma w(|F_0| - |F_c|)^2$ where the weights w were evaluated as $w^{1/2} = 2LpF_0/\sigma(I)$. The agreement factors are defined in the usual manner as

$$R = (\Sigma||F_0| - |F_c||)/(\Sigma|F_0|)$$

and

$$R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2}.$$

Examination of a three dimensional Patterson function indicated the positions of the bromine and phosphorus atoms,

TABLE IV

Experimental data for x-ray diffraction study

(a) Crystal parameters at 21°

$a = 15.528$ (7) Å	Space group Pbca [D_{2h};[15] No. 61]
$b = 16.892$ (7) Å	$Z = 8$
$c = 17.921$ (8) Å	Mol. wt. = 463.36
$V = 4700.4$ Å^3	ρ(calc) = 1.309 g·cm^{-3}
	ρ(obs) = 1.308 g·cm^{-3}

(b) Measurement of intensity data

Radiation: MoKα (Zr filter)
Attenuators: Nickel foil. Total of 4 used-factors (F) ranged from 1.50 to 12.10
Take off angle: 3.5°
Detector aperture: 1.2 mm diameter
Incident beam collimator: 0.9 mm diameter
Crystal-detector distance: 98 mm
Crystal orientation: roughly aligned on [110]
Reflections measured: $+h, +k, +l$
Maximum 2θ: 42°
Scan type: coupled θ-2θ
Scan speed: 10°/min.
Scan range: $\Delta(2\theta) = (0.80 + 0.30 \tan\theta)°$ centered about average peak position
Background measurement: stationary crystal, stationary counter; one half scan time at beginning and end of 2θ scan.
Standard reflection: One, (331), measured every 50 reflections. No significant deviation from average.
Reflections collected: $+h, +k, +l$; 2192 independent reflections. Approximately 200 symmetry related reflections measured.

(c) Treatment of intensity data

Conversion to I and $\sigma(I)$:
$I = [P - (B_1 + B_2)](F/n_s)$
P = Total count; B = Background
$\sigma(I) = [(P + B_1 + B_2)(F/n_s)^2 + (cI)^2]^{1/2}$
'Ignorance Factor' $c = 0.04$
Absorption coefficient: $\mu = 19.2$ cm^{-1}; No absorption corrections applied (see text).

and a structure factor calculation based on these atoms gave $R = 0.48$ and R_w (unit weights) = 0.53. The remaining 27 non-hydrogen atoms were located in three successive electron density maps and full matrix least squares refinement with isotropic thermal parameters led to residuals of 0.179 and 0.303 for all 2192 reflections measured, after three cycles. Examination of individual structure factors indicated rather poor agreement for the majority of those reflections which had a negative net count. In the data reduction calculation these had been given F_0 values based on their σ(I)'s. These reflections, a total of 435 in number, were therefore given zero weight in further refinement and the residuals based on the remaining 1757 reflections were 0.133 and 0.182 respectively. Anisotropic refinement was then undertaken, treating initially the bromine and phosphorus, and then all remaining atoms; and one complete cycle (made up from two "half" cycles in each of which two groups plus the phosphorus were refined) led to R factors of 0.124 and 0.159. A difference electron density map calculated at this stage indicated plausible positions for several of the phenyl ring hydrogen atoms, and it was therefore decided to include all

TABLE V

Atomic coordinates for $P(C_6H_5)_2(CH_2C_6H_5)(C_6H_4OCH_3)^+Br^-$ (Standard deviations in parentheses)

	X	Y	Z
Br	0.0420 (1)	0.1516 (1)	0.0933 (1)
P	0.2069 (3)	0.5021 (2)	0.4374 (2)
C(11)	0.2166 (10)	0.5679 (8)	0.5159 (7)
C(12)	0.2932 (11)	0.6087 (9)	0.5317 (9)
C(13)	0.3028 (11)	0.6571 (9)	0.5922 (9)
C(14)	0.2368 (11)	0.6640 (10)	0.6436 (8)
C(15)	0.1603 (11)	0.6250 (9)	0.6322 (9)
C(16)	0.1503 (10)	0.5786 (9)	0.0038 (8)
O	0.3571 (8)	0.5917 (6)	0.4790 (6)
CME	0.4370 (14)	0.6339 (19)	0.4909 (14)
C(21)	0.2349 (10)	0.5554 (8)	0.3512 (7)
C(22)	0.1762 (10)	0.6064 (10)	0.3232 (9)
C(23)	0.1931 (13)	0.6479 (11)	0.2571 (10)
C(24)	0.2689 (13)	0.6333 (10)	0.2212 (10)
C(25)	0.3296 (13)	0.5845 (11)	0.2493 (11)
C(26)	0.3139 (12)	0.5434 (12)	0.3164 (12)
C(31)	0.2745 (9)	0.4151 (9)	0.4513 (10)
C(32)	0.3007 (13)	0.3611 (11)	0.3950 (9)
C(33)	0.3476 (14)	0.2956 (11)	0.4075 (14)
C(34)	0.3693 (13)	0.2778 (9)	0.4768 (15)
C(35)	0.3454 (12)	0.3222 (12)	0.5320 (11)
C(36)	0.2982 (12)	0.3910 (9)	0.5211 (10)
CBZ	0.0959 (9)	0.4691 (7)	0.4315 (7)
C(41)	0.0777 (8)	0.4089 (8)	0.3683 (8)
C(42)	0.0523 (10)	0.4344 (10)	0.2993 (10)
C(43)	0.0387 (12)	0.3688 (15)	0.2438 (10)
C(44)	0.0523 (15)	0.2946 (12)	0.2647 (17)
C(45)	0.0764 (18)	0.2723 (11)	0.3318 (13)
C(46)	0.0864 (12)	0.3301 (8)	0.3798 (9)

hydrogen atoms, as fixed contributions to the structure factors, each with a B value equal to the isotropic value for the carbon to which it is bonded. Three further cycles of anisotropic refinement including the hydrogens led to convergence and to final unweighted and weighted R values of 0.089 and 0.120 respectively for the 1757 reflections, and to $R = 0.149$ and $R_w = 0.135$ for all reflections. No parameter shift was greater than 20% of the corresponding e.s.d. in the final cycle, and the value for the standard deviation of an observation of unit weight was 0.890 at the end of refinement. The positional and thermal parameters derived from the final cycle along with their e.s.d.'s are listed in Tables V and VI. A compilation of observed and calculated structure factors is available.[19]

Molecular Mechanics Calculations. These calculations were carried out using a version of the molecular mechanics program MMI, written by N. L. Allinger *et al.*[20] and adapted for local use.[21] The object of the calculation was to examine the geometry of the phosphonium cation predicted by the minimization of the total bond stretching and angle bending energies and the van der Waals non-bonded interaction energy, both including and excluding a P–O bonding interaction. The expression used for the total steric energy E_{TOT} was $E_{TOT} = \Sigma E_{STR} + \Sigma E_{BEND} + \Sigma E_{TOR} + \Sigma E_{N.B}$ where $E_{N.B}$ are the van der Waals non-bonded interactions. Force constants for the bonds involving phosphorus were taken from Ref. 21, and Badgers rule[22] was used to obtain a value of 0.30 m · dyn/Å for the long P–O distance. As a starting point for the calculations, an orthogonal set of atom coordinates was used in order that a minimum energy geometry related to that crystallographically observed might be produced. Small deviations from the crystal coordinates were also permitted and the minimization calculations rerun. However, convergence in these cases gave geometries virtually indistinguishable from those obtained with the initial set of coordinates.

ACKNOWLEDGEMENT

This work was supported in part by a grant from the National Science Foundation. We thank the University Computing Center for provision of a generous allocation of computer time.

REFERENCES AND NOTES

1. W. E. McEwen, J. E. Fountaine, D. N. Schulz and W. I. Shiau, *J. Org. Chem.* **41**, 1684 (1976).
2. W. E. McEwen, W. I. Shiau, Y. I. Yeh, D. N. Schulz, R. U. Pagilagan, J. B. Levy, C. Symmes, Jr., G. O. Nelson and I. Granoth, *J. Am. Chem. Soc.* **97**, 1787 (1975).
3. W. E. McEwen, V. L. Kyllingstad, D. N. Schulz and Y. I. Yeh, *Phosphorus* **1**, 145 (1971).
4. Schulz has suggested that the rate acceleration might be the result of a polarization of the lone pair of electrons on phosphorus caused by a repulsion interaction with a pair of 2*p* electrons on the methoxy group.[5] Of course,

TABLE VI

Thermal parameters[a] for $P(C_6H_5)_2(C_6H_5CH_2)(C_6H_4OCH_3)^+Br^-$ (standard deviations in parentheses)

Atom	β_{11}[b]	β_{22}	β_{32}	β_{12}	β_{13}	β_{23}
Br	41.6 (9)	39.2 (8)	31.1 (7)	1.3 (6)	−4.4 (6)	−5.6 (6)
P	33.1 (20)	26.3 (16)	24.2 (15)	−0.4 (16)	4.5 (15)	−4.0 (13)
C(11)	44 (9)	33 (7)	23 (6)	−3 (7)	11 (6)	2 (5)
C(12)	42 (9)	52 (8)	38 (7)	−6 (7)	21 (7)	10 (6)
C(13)	66 (10)	43 (7)	36 (7)	−15 (7)	−10 (8)	−20 (6)
C(14)	56 (10)	68 (10)	29 (6)	−1 (8)	−6 (7)	−21 (6)
C(15)	74 (11)	47 (7)	31 (7)	−21 (7)	−3 (7)	−32 (6)
C(16)	38 (8)	49 (8)	42 (7)	−5 (7)	15 (6)	8 (6)
O	51 (7)	71 (6)	46 (5)	−21 (5)	−4 (5)	−18 (5)
CME	51 (14)	221 (27)	77 (13)	−73 (17)	−1 (11)	−20 (15)
C(21)	47 (9)	33 (6)	15 (5)	−7 (6)	9 (6)	−1 (5)
C(22)	38 (9)	51 (8)	36 (7)	21 (7)	14 (6)	14 (7)
C(23)	69 (13)	62 (10)	27 (7)	14 (9)	21 (8)	13 (7)
C(24)	65 (12)	39 (8)	35 (7)	0 (8)	10 (8)	10 (6)
C(25)	69 (12)	63 (10)	40 (8)	−20 (10)	35 (8)	5 (8)
C(26)	41 (11)	74 (11)	63 (10)	5 (8)	7 (8)	−1 (9)
C(31)	30 (8)	51 (7)	43 (7)	4 (6)	−1 (6)	−5 (7)
C(32)	82 (12)	66 (10)	31 (6)	−19 (9)	16 (7)	−12 (7)
C(33)	75 (13)	46 (9)	73 (12)	23 (8)	23 (10)	−15 (9)
C(34)	84 (13)	33 (8)	67 (10)	13 (8)	16 (10)	−10 (8)
C(35)	74 (12)	51 (10)	51 (9)	23 (9)	−6 (8)	29 (8)
C(36)	67 (10)	55 (8)	33 (8)	1 (8)	5 (7)	9 (6)
CBZ	40 (8)	32 (6)	31 (6)	−7 (6)	0 (5)	3 (5)
C(41)	35 (7)	40 (7)	28 (6)	2 (6)	5 (5)	−11 (5)
C(42)	39 (9)	73 (10)	46 (8)	4 (8)	6 (7)	−4 (8)
C(43)	68 (11)	162 (17)	21 (7)	−53 (13)	1 (7)	−35 (10)
C(44)	107 (15)	35 (10)	113 (16)	−38 (11)	45 (13)	−20 (11)
C(45)	184 (21)	35 (9)	60 (10)	−10 (10)	40 (13)	−16 (9)
C(46)	96 (12)	36 (7)	56 (7)	−4 (7)	20 (8)	−12 (6)

[a] The form of the thermal ellipsoid is $\exp[-\Sigma_i\Sigma_j h_i h_j \beta_{ij}]$ with $i,j = 1, 2, 3$.
[b] Values multiplied by 104.

at some point during the course of the reaction, this type of interaction would become a partially bonding one as the phosphorus becomes positively charged. However, such a changeover in the nature of the interaction would not necessarily coincide with the transition state of the reaction. McEwen *et al.*[2] also pointed out that the influence of the *o*-methoxy group may be partly or completely the result of a field effect rather than an overlap effect.

5. D. N. Schulz, Ph.D. Dissertation, University of Massachusetts, Amherst, Massachusetts, 1971, p. 81.
6. T. K. Khotsyanova and Yu. T. Stinchov, *Soviets Physics Crystallography* **1**, 527 (1956).
7. A. R. Alkaraghouli and J. S. Wood, *J. Chem. Soc. Dalton Trans.* 2318 (1973).
8. J. J. Daly and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1703 (1966).
9. J. J. Daly and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1913 (1967).
10. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960, p. 260.
11. I. Kawamoto, T. Hata, Y. Kishida and C. Tamura, *Tetrahedron Letters*, 1611 (1972).
12. G. Ferguson and D. F. Rendle, *J. Chem. Soc. Dalton Trans.*, 1284 (1975).
13. F. C. March, G. Ferguson and D. Lloyd, *J. Chem. Soc. Dalton Trans.*, 1377 (1975).
14. L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., Pergamon Press, London, 1969, pp. 80–81 and 94–98.
15. One of a package of programs including cell refinement and data collection routines supplied by Enraf-Nonius Inc. for the CAD-3 automatic diffractometer.
16. Assuming indices for the various crystal faces, absorption corrections for a selection of reflections were calculated and these confirmed the conclusions regarding relative intensities obtained from ϕ scans. The transmission factors in this sample calculation varied from 1659 to 0.741.
17. D. T. Crome and J. T. Waber, *Acta Crystallogr.* **18**, 104 (1965).
18. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* **42**, 3175 (1965).
19. See paragraph at end of paper regarding supplementary material.
20. N. L. Allinger, M. T. Tribble, M. A. Miller and D. H. Wertz, *J. Am. Chem. Soc.* **93**, 1637 (1971).
21. For a description of local modifications and adaption to the CDC-6600 computer, see "Computer simulation of phosphorane structures" by T. E. Clark, Sister R. M. Deiters, and R. R. Holmes; submitted for publication.
22. R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

Table of observed and calculated structure factors for benzyl-(2-methoxyphenyl)diphenylphosphonium bromide (Values in electrons x 10) is available.