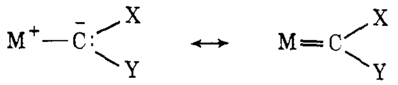
The Structure of Triphenylphosphonium Cyclopentadienylide. An Evaluation of Ylene–Ylide Character from Structural Data

Herman L. Ammon,* George L. Wheeler, and Plato H. Watts, Jr.

Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742. *Received February 5, 1973*

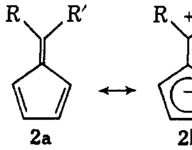
Abstract: The crystal structure of triphenylphosphonium cyclopentadienylide has been determined from an X-ray crystallographic investigation. Mo Kα radiation was used and the X-ray intensities were measured with a computer-controlled diffractometer. The space group is monoclinic, $P2_1/n$; the lattice constants are a = 10.564, b = 8.986, c = 18.708 Å, β = 93.41°; there are four molecules per cell. The amount of ylene–ylide character (*ca.* 20–80%) is estimated from the P–C bond length, the π-electron delocalization in the five ring evaluated from the C–C distances, and from the plus charge on P obtained from the P photoelectron spectrum. These data are compared with the results from a previously reported MO analysis. The conformations about the P–C (five ring) bond in the compound and about the P–C$^-$ bonds in a number of other ylides can be explained in terms of the orientations necessary for C p-orbital overlap with the two P d orbitals of π symmetry.

The term "ylide"[1] is used to describe a class of nitrogen-, phosphorus-, or sulfur-containing organic compounds which have the general structure illustrated in **1**. In many ylides, X and/or Y are electron withdrawing groups. The identity of M might be pyridine in the case of a N ylide, Ph_3P in a P ylide, or Me_2S in a S ylide. The stability of these compounds, which depends on the delocalization of the minus charge in the dipolar form (**1a**), is related to the electron withdrawing characteristics of X and Y and to the degree of double bond formation between M^+ and C^- (**1b**). Since M in structure **1a** already has a filled (8 e) valence shell, any further interaction with the C's unshared pair of electrons must occur *via* dπ–pπ overlap. This type of interaction may be important in the S and P ylides, especially if electron delocalization to X and Y is small.

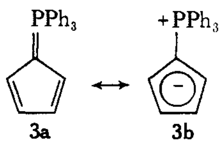


1a 1b

The cyclopentadienylides were of interest to us because the five-ring structure could serve as a model for the dipolar canonical form, **2b**, in the pentafulvenes (**2**). Triphenylphosphonium cyclopentadienylide (**3**) was especially attractive in this respect because of its high dipole moment, 6.99 D,[2] and because a combined spectroscopic–MO investigation of the tri-*n*-propyl derivative[3] had partitioned the ground state hybrid into 16% ylene (like **3a**) and 84% ylide (like **3b**). Furthermore, **3** was known to be stable and quite unreactive for an ylide.



2a 2b



3a 3b

The results of an X-ray crystallographic analysis of triphenylphosphonium cyclopentadienylide (**3**) and the determination of its phosphorus 2p photoelectron spectrum are reported and discussed in this paper. Estimates of the amounts of ylene–ylide character from MO calculations,[3] the P–C (five ring) distance, and five-ring bond lengths are in excellent agreement.

Experimental Section

Triphenylphosphonium cyclopentadienylide (PCYCLO) was synthesized *via* the triphenylphosphine–dibromocyclopentene route of Ramirez and Levy.[2] After a number of recrystallization solvents were tried, toluene was found to give crystals which were suitable both in the size and quality necessary for an X-ray diffraction analysis.

X-Ray Data Collection. The Laue symmetry, systematic absences, and rough values of the lattice constants were obtained from X-ray photographs. The final cell parameter and all intensity measurements were made using monochromatic Mo Kα radiation (by diffraction from a highly oriented graphite crystal, λ 0.71069 Å) and a Picker FACS-I diffractometer. The crystal, a cube *ca.* 0.3 mm on a side, was mounted and aligned to place b^* parallel to the instrument's ϕ axis. The cell constants were calculated by the method of least squares using twelve 2θ angles determined from manual measurements of $+2\theta$ and -2θ for each reflection; the average of $|2\theta_o - 2\theta_c|$ was 0.003°. The space group is monoclinic, $P2_1/n$, and the cell parameters are a = 10.564 (1), b = 8.986 (1), c = 18.708 (2) Å, β = 93.41 (1)°. The measured crystal density is 1.221 g cm^{-3} (aqueous KI) and the calculated value for Z = 4 is 1.223 g cm^{-3}.

The intensity data were measured using the θ–2θ scan method at a rate of 0.5° min^{-1} over a 2θ range computed from 1.6 + 0.70° tan θ; 40-sec background measurements were made at the start and finish of each scan. Three standard reflections were measured every 80 reflections to monitor intensity fluctuations and the sample was manually centered and realigned every 2 days. Metal foil X-ray attenuators were automatically inserted into the diffracted beam to keep the maximum count rate below about 15,000 counts sec^{-1}. A total of 3642 data were measured to a 2θ maximum of 50°. Of the data, 3353 (including 223 systematic absences) were unique and 2494 were 3σ above background and coded "observed." The reflection intensities (I) and standard deviations ($\sigma(I)$) were calculated from

$$I = SA(I_S - K(I_{B1} + I_{B2}))$$

$$\sigma(I) = (S^2A^2(I_S + K^2(I_{B1} + I_{B2})) + DC^2)^{1/2}$$

I_S is the scan count; I_{B1} and I_{B2} are the background counts; K = (scan time in sec)/80; S is a scale factor obtained from the standard reflection data; A is the attenuator factor; $C = I_S + I_{B1} + I_{B2}$; and D (0.00022 for PCYCLO) is an experimental instrumental instability factor[4] obtained from the variations in the standard reflection intensities. The linear absorption coefficient is 1.59 cm^{-1}. Absorption corrections were not made.

---

(1) G. Wittig and G. Felletschin, *Justus Liebigs Ann. Chem.*, **555**, 133 (1944).

(2) F. Ramirez and S. Levy, *J. Amer. Chem. Soc.*, 79, 6167 (1957).

(3) K. Iwata, S. Yoneda, and Z. Yoshida, *ibid.*, **93**, 6745 (1971).

(4) G. H. Stout and L. H. Jensen, "X-ray Structure Determination, A Practical Guide," Macmillan, New York, N. Y., 1968, p 456.

Table I. Fractional Atomic Coordinates and Temperature Factors (Å^2)^a for Triphenylphosphonium Cyclopentadienylide

Atom	X	Y	Z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	0.27082 (6)	0.38064 (7)	0.08891 (3)	0.0411 (3)	0.0377 (3)	0.0375 (3)	0.0022 (3)	0.0042 (2)	0.0009 (3)
C(1)	0.4118 (2)	0.3402 (3)	0.1354 (1)	0.048 (1)	0.043 (1)	0.041 (1)	0.005 (1)	0.001 (1)	−0.001 (1)
C(2)	0.4447 (2)	0.1994 (3)	0.1668 (1)	0.068 (2)	0.048 (2)	0.052 (2)	0.004 (1)	−0.004 (1)	0.002 (1)
C(3)	0.5749 (3)	0.2022 (3)	0.1836 (1)	0.069 (2)	0.063 (2)	0.047 (1)	0.023 (2)	−0.009 (1)	−0.007 (1)
C(4)	0.6232 (2)	0.3398 (3)	0.1627 (1)	0.049 (2)	0.081 (2)	0.056 (2)	0.007 (1)	0.000 (1)	−0.009 (2)
C(5)	0.5251 (2)	0.4241 (3)	0.1327 (1)	0.045 (1)	0.053 (2)	0.048 (1)	0.003 (1)	0.003 (1)	−0.004 (1)
C(1A)	0.1409 (2)	0.2948 (3)	0.1316 (1)	0.045 (1)	0.043 (1)	0.044 (1)	0.005 (1)	0.006 (1)	0.006 (1)
C(2A)	0.1489 (2)	0.2880 (3)	0.2066 (1)	0.062 (2)	0.091 (2)	0.048 (2)	−0.010 (2)	0.009 (1)	0.011 (2)
C(3A)	0.0523 (3)	0.2190 (4)	0.2416 (2)	0.071 (2)	0.127 (3)	0.058 (2)	−0.004 (2)	0.019 (2)	0.027 (2)
C(4A)	−0.0504 (3)	0.1575 (4)	0.2034 (2)	0.054 (2)	0.094 (3)	0.084 (2)	0.001 (2)	0.020 (2)	0.028 (2)
C(5A)	−0.0590 (2)	0.1671 (3)	0.1303 (2)	0.047 (2)	0.085 (2)	0.081 (2)	−0.010 (1)	0.006 (1)	0.010 (2)
C(6A)	0.0364 (2)	0.2356 (3)	0.0943 (1)	0.050 (1)	0.061 (2)	0.054 (2)	0.000 (1)	0.006 (1)	0.005 (1)
C(1B)	0.2445 (2)	0.5791 (3)	0.0834 (1)	0.043 (1)	0.039 (1)	0.047 (1)	0.002 (1)	−0.002 (1)	−0.002 (1)
C(2B)	0.3051 (2)	0.6608 (3)	0.0322 (1)	0.063 (2)	0.046 (2)	0.066 (2)	0.002 (1)	0.008 (1)	0.008 (1)
C(3B)	0.2906 (3)	0.8132 (3)	0.0289 (2)	0.074 (2)	0.045 (2)	0.099 (2)	0.000 (1)	0.001 (2)	0.012 (2)
C(4B)	0.2131 (3)	0.8822 (3)	0.0760 (2)	0.075 (2)	0.042 (2)	0.121 (3)	0.002 (2)	−0.019 (2)	−0.001 (2)
C(5B)	0.1521 (3)	0.8038 (3)	0.1263 (2)	0.064 (2)	0.059 (2)	0.096 (2)	0.014 (1)	−0.002 (2)	−0.022 (2)
C(6B)	0.1675 (2)	0.6503 (3)	0.1302 (1)	0.054 (2)	0.053 (2)	0.062 (2)	0.007 (1)	0.005 (1)	−0.007 (1)
C(1C)	0.2663 (2)	0.3150 (3)	−0.0025 (1)	0.045 (1)	0.039 (1)	0.042 (1)	−0.006 (1)	0.008 (1)	−0.001 (1)
C(2C)	0.3555 (2)	0.2085 (3)	−0.0197 (1)	0.063 (2)	0.042 (1)	0.049 (1)	−0.002 (1)	0.013 (1)	0.001 (1)
C(3C)	0.3548 (3)	0.1516 (3)	−0.0893 (2)	0.091 (2)	0.053 (2)	0.060 (2)	−0.006 (2)	0.025 (2)	−0.011 (1)
C(4C)	0.2659 (3)	0.2027 (3)	−0.1404 (1)	0.088 (2)	0.075 (2)	0.045 (2)	−0.026 (2)	0.014 (1)	−0.014 (2)
C(5C)	0.1794 (3)	0.3082 (4)	−0.1240 (1)	0.063 (2)	0.098 (2)	0.045 (2)	−0.012 (2)	−0.003 (1)	0.001 (2)
C(6C)	0.1787 (2)	0.3659 (3)	−0.0554 (1)	0.054 (1)	0.075 (2)	0.044 (1)	0.001 (1)	0.001 (1)	0.000 (1)
H(2)	0.383 (2)	0.119 (3)	0.175 (1)	0.075 (8)					
H(3)	0.626 (2)	0.121 (3)	0.209 (1)	0.075 (8)					
H(4)	0.719 (2)	0.364 (3)	0.168 (1)	0.098 (9)					
H(5)	0.526 (2)	0.524 (2)	0.112 (1)	0.063 (7)					
H(2A)	0.229 (2)	0.337 (3)	0.238 (1)	0.081 (8)					
H(3A)	0.063 (3)	0.215 (3)	0.296 (2)	0.12 (1)					
H(4A)	−0.115 (2)	0.106 (3)	0.234 (1)	0.096 (9)					
H(5A)	−0.128 (2)	0.136 (3)	0.105 (1)	0.088 (9)					
H(6A)	0.027 (2)	0.243 (3)	0.046 (1)	0.066 (8)					
H(2B)	0.371 (2)	0.607 (3)	0.001 (1)	0.084 (8)					
H(3B)	0.345 (2)	0.877 (3)	−0.010 (1)	0.099 (9)					
H(4B)	0.183 (3)	0.992 (4)	0.062 (2)	0.17 (1)					
H(5B)	0.091 (2)	0.852 (3)	0.160 (1)	0.098 (9)					
H(6B)	0.122 (2)	0.597 (3)	0.164 (1)	0.064 (7)					
H(2C)	0.419 (2)	0.169 (3)	0.019 (1)	0.069 (8)					
H(3C)	0.428 (2)	0.068 (3)	−0.099 (1)	0.091 (9)					
H(4C)	0.263 (2)	0.171 (3)	−0.190 (1)	0.072 (8)					
H(5C)	0.124 (2)	0.334 (3)	−0.156 (1)	0.086 (9)					
H(6C)	0.106 (2)	0.445 (3)	−0.038 (1)	0.079 (8)					

^{a} The temperature factors are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})]$.

X-Ray Structure Determination. The data were reduced and scaled, $|E|$'s were calculated, and the phases for 687 reflections (345 +, 342 −) were obtained in a straightforward way, using the direct methods program PHASE.[5] An E map computed with these 687 data revealed the 24 C and P atoms and a structure factor calculation gave an R index ($R = \Sigma|F_o - F_c|/\Sigma F_o$) of 0.21.

X-Ray Structure Refinement. The structure was refined using the method of full matrix least squares. The calculations minimized the function $\Sigma w(F_o - F_c)^2$; unit weights (w = 1) were used initially, but $1/\sigma^2(F_o)$ weights were applied in the latter refinement cycles. The "unobserved" data were included in the calculations only in those cases in which I_c was greater than $3\sigma(I_o)$. Hydrogen atoms were located in a difference map. The last stages of refinement used anisotropic temperature factors for C and P, isotropic terms for H, and included a correction for isotropic secondary extinction (r^* = 0.0034 (1)).[6] The final R index was 0.042; the weighted R index $((\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2})$ was 0.045. The atomic parameters are listed in Table I. The calculated and observed structure factors will appear as Table II following these pages in the microfilm edition of this volume of the journal. See paragraph at end of paper regarding supplementary material.

X-Ray f Curves. The scattering factor data of Cromer and Mann[7] were used for C and P; the Stewart, Davidson, and Simpson[8] data were used for H.

ESCA. The photoelectron spectra were obtained using a Varian IEE-15 spectrometer, equipped with an Mg X-ray source (K_α, 1253.6 eV). All samples were run at room temperature as powders which were mixed with alumina and dusted onto double-backed cellophane tape. The spectra were referenced to a 73.55 eV Al(2p) line, which had been previously calibrated using gold decoration as the reference (Au $4f_{7/2}$ = 83.0 eV). The phosphorus 2p data reported in Table III are the average values from three or more runs

Table III. Phosphorus 2p Electron Energies^a

Compound	Energy, eV
Triphenylphosphonium cyclopentadienylide	129.6
Triphenylphosphonium fluorenylide	129.2
Triphenylphosphine	127.6
Methyltriphenylphosphonium bromide	130.5

^{a} Each energy is an average of at least three measurements.

---

(5) All calculations were done on a Univac 1108 at the University's Computer Science Center. The X-ray crystallographic programs used were from "The X-ray System-Version of June 1972," Technical Report 192 of the Computer Science Center, University of Maryland, June 1972.

(6) The definition of the secondary extinction parameter r^* and its use in F_c corrections are given in eq 19 and 22 in A. C. Larson, "Crystallographic Computing," F. R. Ahmed, S. R. Hall, and C. P. Huber, Ed., Munksgaard, Copenhagen, 1970, p 291.

(7) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

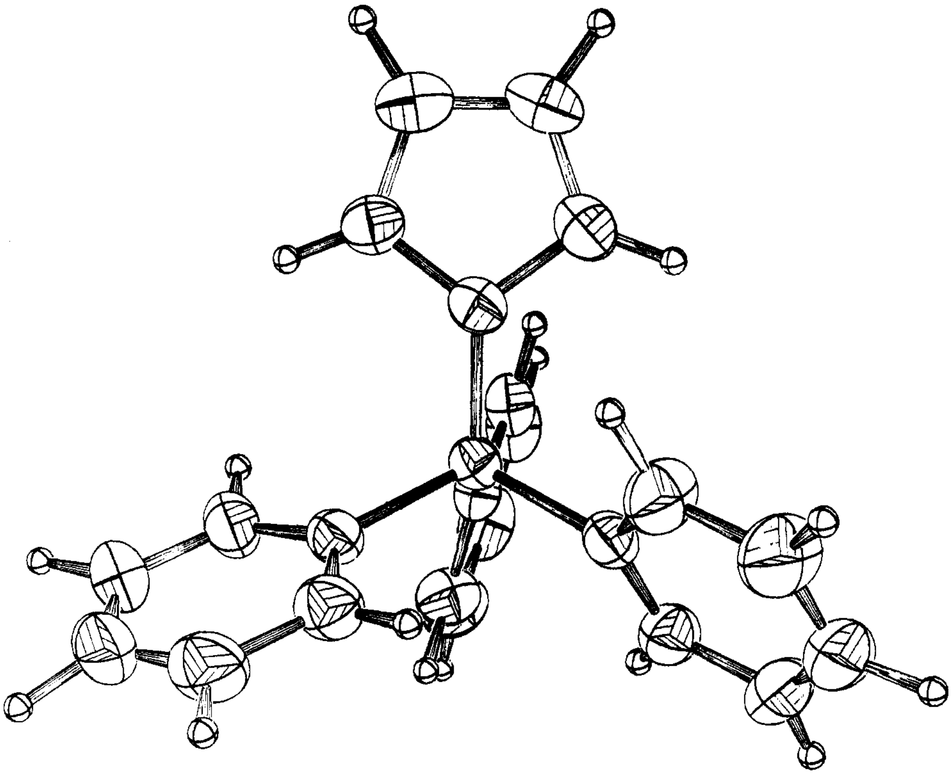


Figure 1. ORTEP-II drawing of PCYCLO. The view is from above the P atom and the five-ring is parallel to the plane of the paper. 45% probability ellipsoids were used for C and P; a sphere of radius 0.1 Å was used for H. The a, b, and c benzene rings are the right most, left most, and lowest rings in the drawing.

for each compound. The spectra were obtained from commercial samples of triphenylphosphonium cyclopentadienylide, triphenylphosphonium fluorenylide (both from Aldrich), and triphenylphosphine (M & T Chemicals, Rahway, N. J.). The methyltriphenylphosphonium bromide was provided by Professor S. O. Grim of our department.

Discussion

Molecular Conformation, Bond Lengths, and Angles. An ORTEP-II drawing[9] illustrating the molecular conformation is shown in Figure 1, and bond lengths and angles are presented in Figure 2. The cyclopentadienylidene and three phenyl rings are each coplanar. The P atom is coplanar with each of the phenyls, but deviates by 0.34 Å from the five-ring plane (see Table IV). There is an almost perfect staggering of the five-ring and the three P–C(Ph) bonds and, with the five-ring as a reference point, it appears that the P–C(Ph) torsion angles have values which minimize intramolecular crowding. The bond lengths, angles, and other parameters in the Ph_3P–C portion of the molecule have values close to those observed in a number of other triphenylphosphonium ylides.[10] Examples of these similarities are: (a) the P–C(Ph) distances, average 1.806 Å, are considerably longer than the ylide phosphorus–carbon bond, P–C(5 ring) = 1.718 Å; (b) the average C(Ph)–P–C(5 ring) angle, 111.4°, is larger than the average C(Ph)–P–C(Ph) angle, 107.5°; (c) the average benzene C–C distances, 1.384, 1.383, and 1.385 Å in rings a, b, and c, are smaller than the standard benzene length of 1.398 Å. The benzene ring distances are undoubtedly shortened by (uncorrected) thermal motion effects since the C temperature factors increase as the atom gets further from the stabilizing P, and the associated C–C distances become smaller.

Table IV. Least-Squares Planes and Deviations for PCYCLO

	Deviations, Å[a]			
Atom	Plane 1	Plane 2	Plane 3	Plane 4
P	−0.337	−0.059	0.061	−0.037
C(1)	0.007*	−1.029	1.660	0.417
C(2)	−0.005*			
C(3)	0.001*			
C(4)	0.004*			
C(5)	−0.007*			
C(1a)	0.391	−0.009*	−0.578	−1.709
C(2a)		0.005*		
C(3a)		0.005*		
C(4a)		−0.010*		
C(5a)		0.005*		
C(6a)		0.004*		
C(1b)	0.298	1.626	0.003*	1.098
C(2b)			−0.006*	
C(3b)			0.005*	
C(4b)			−0.002*	
C(5b)			−0.001*	
C(6b)			0.000*	
C(1c)	−2.111	−0.683	−1.080	−0.007*
C(2c)				0.004*
C(3c)				0.002*
C(4c)				−0.004*
C(5c)				0.001*
C(6c)				0.005*

[a] The asterisks indicate those atoms used to define the planes. Plane 1: $-2.2220x + 3.3827y + 17.0840z = 2.5416$. Plane 2: $-0.4828x + 0.8744y + 0.0482z = 1.7968$. Plane 3: $7.9250x + 1.0770y + 11.3066z = 3.5001$. Plane 4: $6.8394x + 6.4807y - 5.3226z = 3.8832$.

Ylide Character. The most interesting aspects of the

---

[9] C. K. Johnson, ORTEP-II, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[10] These common features have been tabulated in two recent papers: (a) J. C. J. Bart, *J. Chem. Soc. B*, 350 (1969); (b) A. T. Vincent and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 617 (1972).

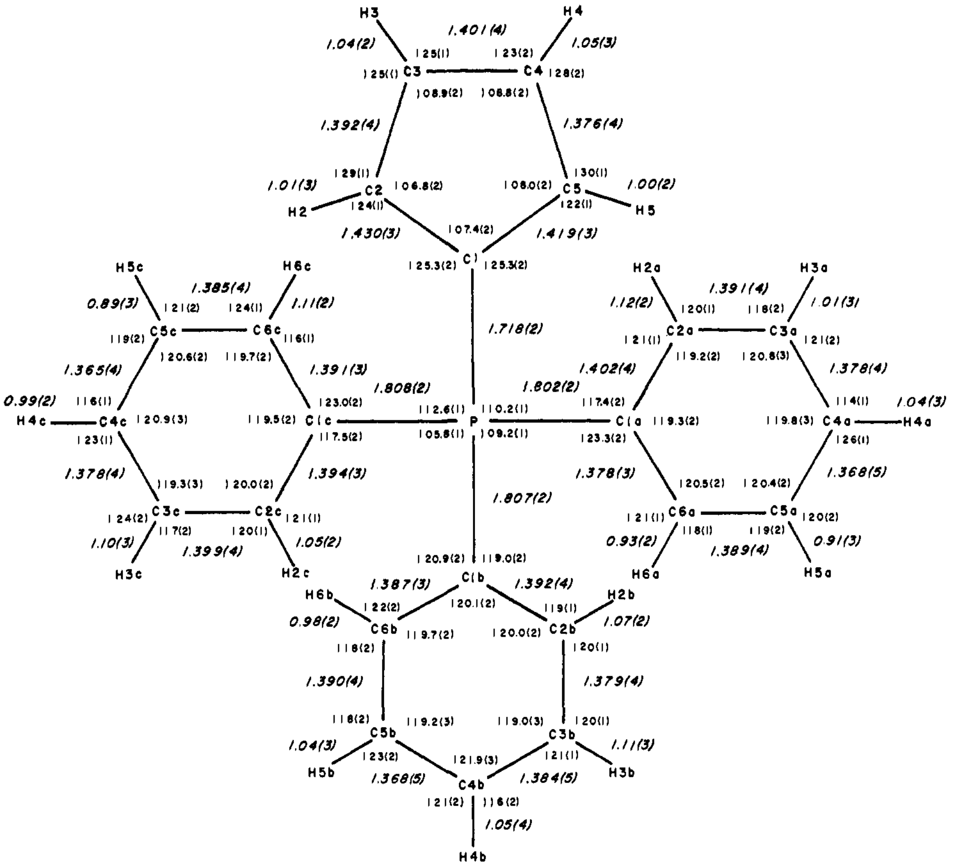


Figure 2. Bond lengths (Å) and angles for PCYCLO. Esd's are given in parentheses. The two P angles not included are C(1)–P–C(1b) = 111.3 (1)° and C(1a)–P–C(1c) = 107.6 (1)°.

structure undoubtedly are associated with the length of the P–C(5 ring) bond, the extent of π-electron delocalization in the five ring, and what these things mean in terms of ground state ylene–ylide character. Any analysis of the percentage of phosphorus–carbon double bond character, deduced from the P–C(5 ring) distance, must rely on a definition of standard lengths for the P—C and P=C bonds. The shortest ylide P–C distances have been reported for $Ph_3P{=}C{=}C{=}O$ (1.648 Å[11]) and $Ph_3P{=}C{=}PPh_3$ (1.631 Å[10b]). These compounds might be termed "sp ylides" because the ylide C is connected to only two other atoms and, from a consideration of the P–C–C and P–C–P angles, the formal hybridization of the C is probably between sp and sp^2. It is inappropriate to use these P–C values as the minimum length for an "sp^2 ylide" like PCYCLO, where the central C is connected to three atoms and the hybridization is sp^2. The best example of an sp^2 ylide with a substantial amount of P=C character is triphenylphosphonium methylide, $Ph_3P{=}CH_2$.[10a] However, even in this compound, with the relatively short P–C distance of 1.66 Å, one cannot assume that the distance represents a pure P=C(sp^2) connection. From a P–C bond force constant analysis, Siebert[12] estimated a bond order of 1.3 for the P–CH$_2$ connection, and, in his discussion of the X-ray results for the methylide, Bart[10a] suggested that any phosphorus–carbon π bond would be polar and he cautioned against exaggeration of the formal differences between the dipolar and double bonded canonical forms. Nevertheless, the methylide appears to be the best benchmark compound available for the P=C(sp^2) end of the scale, while an adequate representation of the P–C(sp^2) distance (1.83 Å[13]) can be obtained from triphenylphosphine. Using the $Ph_3P{=}CH_2$ and Ph_3P data to provide a correlation between phosphorus–carbon distance and single–double bond character, the 1.718 Å P–C(5 ring) distance in PCYCLO gave 34% **3b** using 1.0 for the methylide π-bond order, whereas the quite different result of 80% **3b** was obtained using Siebert's 0.3 methylide π-bond order.[12]

The percentage of dipolar character also should be available from a determination of the excess of plus or minus charge in the two halves of the ylide. We have estimated the amount of plus charge on phosphorus from the magnitude of the binding energy of the P(2p) electrons measured by X-ray photoelectron spectroscopy (ESCA). Our approach was similar to the one recently used by Swartz, Ruff, and Hercules,[14] who concluded that the single best structure for the bis(triphenylphosphine)iminium cation was $Ph_3P(+)$–$N(-)$–$P(+)Ph_3$. We measured the P(2p) electron binding energies for PCYCLO, triphenylphosphine (Ph_3P), and methyltriphenylphosphonium bromide ($Me{-}P{-}Ph_3{}^+Br^-$) to establish energy benchmarks for P compounds with formal charges of 0 and +1 (Table III). Assuming that the P(2p) binding energy and P

---

[11] J. J. Daly and P. J. Wheatley, *J. Chem. Soc. A*, 1703 (1966).

[12] H. Siebert, *Z. Anorg. Chem.*, 273, 170 (1953).

[13] The average C–P distance in triphenylphosphine is 1.828 Å: J. J. Daly, *J. Chem. Soc.*, 3799 (1964); and in tri-*o*-tolylphosphine the average is 1.83 Å: R. A. Shaw, M. Woods, T. S. Cameron, and B. Dahlen, *Chem. Ind. (London)*, 151 (1971).

[14] W. E. Swartz, J. K. Ruff, and D. M. Hercules, *J. Amer. Chem. Soc.*, **94**, 5227 (1972).

plus charge are proportional to each other, these data gave a charge of +0.69 for the P atom in PCYCLO. A binding energy measurement and similar calculation for triphenylphosphonium fluorenylide gave a P charge of +0.55. This value is smaller than the cyclopentadienylide quantity and agrees qualitatively with what one would expect from the relative basicities of cyclopentadienide ($\mathrm{p}K_a$ = 17[15]) and fluorenide ($\mathrm{p}K_a$ = 25[16]). The $\mathrm{p}K_a$'s suggest that π-electron delocalization is more extensive in cyclopentadienide than fluorenide and therefore the cyclopentadienylide should have a smaller excess of electron density for π-bond formation with P and a larger plus charge on P than the fluorenylide.[16a]

The extent of π-electron delocalization in the five ring of PCYCLO can also provide some information on the dipolar–nonpolar question. Our X-ray data do not, of course, give a direct measurement of the atomic electron densities, but some idea of the overall delocalization picture can be gained from the five-ring bond lengths. Previously, we had compared, for several of the pentafulvenes, the double and single carbon–carbon distances in the C=C—C=C portion of the ring to nmr coupling constants between adjacent (vicinal) protons in the same portion of the ring.[17] The difference in the HC=CH and HC—CH coupling constants in PCYCLO, 1.04 Hz ($J_{23} = J_{45} = 3.84$ Hz; $J_{34} = 2.80$ Hz),[18] is among the smallest of these values which have been determined for a variety of cyclopentadiene derivatives. These coupling constant differences have been related to π-bond order[18,19] and bond length[17] differences and thereby to five-ring delocalization. The five-ring charge (q) in PCYCLO can be estimated from the five-ring bond length difference, Δd = (C—C) − (C=C), using the Δd and q values from cyclopentadienide and cyclopentadiene as standards. With these cyclopentadienide ($\Delta d = 0$, $q = -1$) and cyclopentadiene ($\Delta d = 0.127$ Å,[20] $q = 0$) data as end points, and with the assumption of a linear relationship between Δd and q, the Δd of 0.017 Å in PCYCLO corresponds to a five-ring charge (q) of −0.86.[21] This in turn corresponds to an 86% contribution of structure **3b** to the ground state of the compound.

Considerable five-ring π-electron delocalization has been predicted for tri-*n*-propylphosphonium cyclopentadienylide by Iwata, Yoneda, and Yoshida.[3] They used a combination of uv spectroscopy and semiempirical MO techniques to determine a figure of 84% for the dipolar contribution (**3b**) to the ground state. This figure is in excellent agreement with the 80% estimated from the P–C distance and 86% obtained from the five-ring bond lengths.

The accord between these three values lends indirect support for Siebert's 0.3 π-bond order[12] in $Ph_3P{=}CH_2$ and enables one to estimate the amount of single–double bond character in other organo phosphorus compounds. For example, the average 1.74 Å phosphorus–carbon distance in the triphenylphosphorins (**4**)[22] corresponds to about 16% P=C character. Furthermore, the extensive π-electron delocalization determined for PCYCLO parallels the lack of reactivity of the compound in the Wittig reaction[23] and ease of electrophilic substitution.[24]

The P–C(1) Conformation. In the first paragraph of the Discussion, the staggered conformation of the five ring and the three P–C(Ph) bonds about the P–C(5 ring) bond was mentioned. These data were obtained by calculating the angle between the P–cyclopentadienylidene plane and the three C(1)–P–C(Ph) planes. We also performed similar calculations for ten other P ylides[25] with surprisingly different results. In each of these cases, the conformation was one in which one of the P–C(Ph) bonds was nearly in the plane of the ylide C. Using the C plane as a reference point for the P–C conformation, the smallest P–C(Ph) dihedral angles ranged from 1.0° in $Ph_3P{=}C{=}C{=}S$ to 10.8° in $Ph_3P{=}CH_2$. The three dihedral angles in PCYCLO were 28.5, 31.7, and 89.1°. While it is unclear to what extent steric factors operating between the Ph_3P and the ylide C's substituents are responsible for conformational control, there is probably some steric influence since the "in plane" P–C(Ph) bond is always found trans to the largest ylide C substituent. In the case of PCYCLO the substituents on either side of the central ylide C (C(2)–H and C(5)–H) have the same steric bulk, and therefore the staggered conformation probably represents an energy minimum.

These two conformations can be simply related to two possible $d\pi$–$p\pi$ bonding arrangements assuming that the phosphorus atom has tetrahedral symmetry (*i.e.*, point group T_d). The tetrahedral field will split the degeneracy of the five 3d orbitals, pushing the d_{xy}, d_{xz}, and d_{yz} to higher energy and the $d_{x^2-y^2}$ and d_{z^2} to lower energy. The first three d orbitals have the correct symmetry for σ-bond formation whereas the remaining two have π-bond symmetry. There are two orientations of the ylide C p orbital (assuming sp^2 hybridization) which will maximize the $d\pi$–$p\pi$ overlap with the P $d_{x^2-y^2}$ and d_{z^2} orbitals. The maximum p–$d_{x^2-y^2}$ interaction requires that the p orbital be perpendicular to one of the C(1)–P–C(Ph) planes whereas the maximum p–d_{z^2} interaction would occur with the p orbital parallel to one of the C(1)–P–C(Ph) planes.

---

(15) D. Peters, *J. Chem. Soc.*, 1274 (1960).

(16) J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, **54**, 1212 (1932).

(16a) NOTE ADDED IN PROOF. These arguments are tentatively supported by the ^{13}C chemical shifts and ^{13}C–^{31}P coupling constants reported by G. A. Gray, *J. Amer. Chem. Soc.*, **95**, 5092 (1973), for triphenylphosphonium cyclopentadienylide (δ = 78.26 ppm, J = 113.1 Hz) and fluorenylide (δ = 53.28 ppm, J = 128.7 Hz).

(17) H. L. Ammon and G. L. Wheeler, *Chem. Commun.*, 1033 (1971); H. L. Ammon, G. L. Wheeler, and L. A. Plastas, Abstracts, American Crystallographic Association Meeting, April 1972, p 30.

(18) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Amer. Chem. Soc.*, **89**, 1438 (1967).

(19) E. E. Ernstbrunner and D. Lloyd, *Chem. Ind.* (*London*), 1332 (1971).

(20) L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965).

(21) A manuscript detailing these kinds of coupling constant–bond length difference–bond order–ring charge relationships and their implications is in preparation.

(22) The average P–C distances in **4** are 1.72 Å, X = Me: V. Thewalt, *Angew. Chem., Int. Ed. Engl.*, **8**, 769 (1969); 1.749 Å, X = Me: J. J. Daly, *J. Chem. Soc. A*, 1832 (1970); and 1.739 Å, X = NMe_2: V. Thewalt and C. E. Bugg, *Acta Crystallogr., Sect. B*, **28**, 871 (1972).

(23) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 70.

(24) Z. Yoshida, S. Yoneda, Y. Murata, and H. Hashimoto, *Tetrahedron Lett.*, 1523 (1971).

(25) $Ph_3P{=}CH_2$, 2 molecules: ref 10a; $Ph_3P{=}C(Cl){-}C({=}O){-}Ph$: F. S. Stephens, *J. Chem. Soc.*, 5658 (1965); $Ph_3P{=}C(I){-}C({=}O){-}Ph$: F. S. Stephens, *ibid.*, 5640 (1965); $Ph_3P{=}CH{-}SO_2{-}Ph{-}Me$: P. J. Wheatley, *J. Chem. Soc.*, 5785 (1965); $(Ph_3P)_2C{-}C(N{-}Ph)_2$: F. K. Ross, W. C. Hamilton, and F. Ramirez, *Acta Crystallogr., Sect. B*, **27**, 2331 (1971); $Ph_3P{=}C{=}PPh_3$; 2 molecules: ref 10b; $Ph_3P{=}C{=}C{=}O$: ref 11; $Ph_3P{=}C{=}C{=}S$: J. J. Daly, *J. Chem. Soc. A*, 1913 (1967).

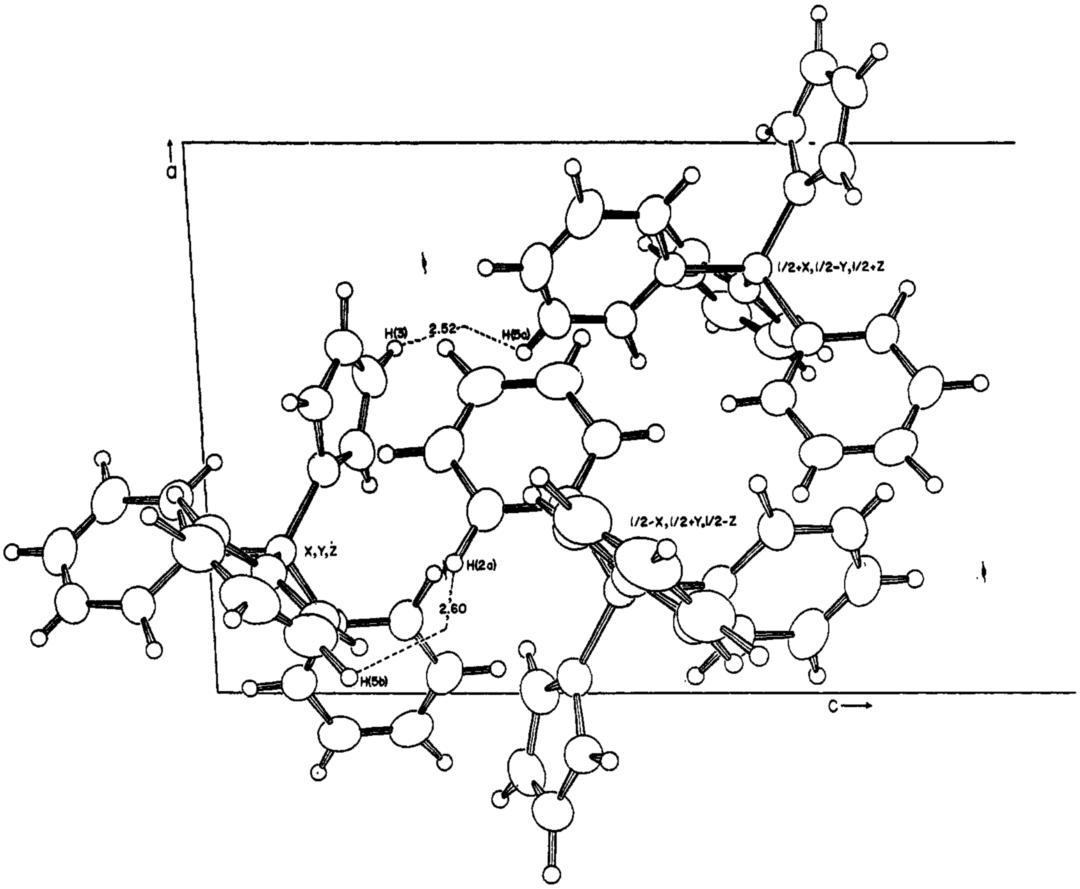


Figure 3. ORTEP-II packing diagram for PCYCLO. The *b* axis is normal to the page.

Since the plane of the ylide C is normal to the p orbital, the maximum p–$d_{x^2-y^2}$ and p–d_{z^2} interactions would occur with the sp^2 plane oriented, respectively, parallel and perpendicular to one of the C(1)–P–C(Ph) planes. These two orientations correspond to the staggered and eclipsed conformations (*vide supra*).

Molecular Packing. A molecular packing diagram drawn with the ORTEP-II program[9] is shown in Figure 3. Since each molecule has a spherical, hydrocarbon-like exterior there are essentially no close intermolecular approaches. The two shortest contacts, H···H, are shown in the figure.

Acknowledgments. This work was supported by the National Science Foundation (GP-15791 and 37528) and, in part, by the Computer Science Center of the University of Maryland through a grant of computer time. The ESCA research was supported by the Center for Materials Research, University of Maryland.

Supplementary Material Available. Table II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementry material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-6158.