

# The Crystal and Molecular Structure of 1,1,4,4-Tetraethyl-2,5-dimethyl-1,4-diphosphoniacyclohexadiene-1,4-dibromide

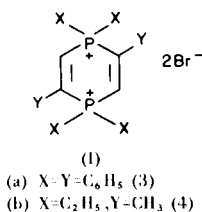
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The structure of the title compound has been determined by a single-crystal, x-ray diffraction study. The compound crystallizes in a monoclinic unit cell ( $P2_1/c$ ) with two molecules per unit cell. Least-squared lattice parameters are:  $a = 7.164 \pm 0.001\text{\AA}$ ,  $b = 14.770 \pm 0.001\text{\AA}$ ,  $c = 10.562 \pm 0.001\text{\AA}$ , and  $\beta = 124.95 \pm 0.01^\circ$ . The structure parameters refined to a value of  $R=0.06_2$ , excluding hydrogens, for the 1475 statistically significant reflections. The structure determination confirmed that the compound is indeed a diene and not a delocalized structure. The ring is planar but the ethyl groups extend over the ring in an unusual crab-like fashion.

## Introduction

The existence and nature of  $\pi$ -electron delocalization in the phosphonitrilic system has resulted in some controversy (1,2). Recently, a series of stable compounds containing such a system (1) have been synthesized (3,4).



Preliminary analysis of the nmr spectrum of one of these, the 1,1,2,4,4,5-hexaphenyl derivative, led to the prediction (5) that the  $\pi$ -electronic charge is extensively delocalized in these systems over the phosphorus atoms. Support for this prediction was obtained from  $^{31}\text{P}$  nmr shifts measured at 40.5 Mc/sec (shifts expressed in parts per million of methanol solutions relative to an external standard of 85%  $\text{H}_3\text{PO}_4$ ). The compound represented the first report of a phosphonium salt with a positive  $^{31}\text{P}$  nmr shift (3.5 cps) compared to the usual large negative shifts (-20 to -30 cps) encountered for simple phosphonium salts.

In order that this controversy regarding the delocalization be resolved and to better understand the bonding in these systems, the crystal and molecular structure of 1b was determined and is herein reported.

## Experimental and Structure Determination

A sample of the title compound was kindly furnished to us by Professor Adam Aguiar of Tulane University.

Unfortunately, attempts to recrystallize the compound resulted either in extremely small rhombohedral crystals (approximately 0.01 mm on each edge) or bulky polycrystalline material. Finally, one of these admittedly inferior larger crystals was mounted and a preliminary data set was collected by precession camera methods. A trial structure, reported earlier (6), was obtained but we were unable to refine it below a value of  $R=0.16$ . All further attempts to recrystallize the sample by a variety of mixed-solvent techniques failed.

As a last resort, apparatus (7) allowing very slow solvent-diffusion was designed and prepared. Our first attempt to recrystallize the sample was successful using acetonitrile as the solvent and ethyl ether as the diffusing liquid. The crystals obtained were beautiful rhombohedral crystals varying in size from 0.1-0.5 mm along the edge. One of the smaller crystals (0.14 x 0.14 x 0.17 mm) was used in all subsequent work.

The crystal was mounted on a G. E. XRD-5 diffractometer and the symmetry and cell data were redetermined using filtered  $\text{Cu K}\alpha$  radiation. The space group was reconfirmed as  $P2_1/c$  and the calculated density of  $1.51_6$  g/cc assuming two molecules per unit cell agreed well with the density of  $1.51$  g/cc determined by flotation methods. The two-theta values of forty-seven reflections of sufficiently high intensity to be observable at fine conditions ( $1^\circ$  take-off angle and  $0.05^\circ$  slit) were measured very carefully and used for a least-squares fit of the lattice constants (8). All of these two-theta values were greater than  $60^\circ$ , and thus the  $\text{K}\alpha_1$  and  $\text{K}\alpha_2$  peaks were resolvable on our instrument. The resulting lattice constants are:

$$a = 7.164 \pm 0.001\text{\AA}$$

$$b = 14.770 \pm 0.001 \text{ \AA}$$

$$c = 10.562 \pm 0.001 \text{ \AA}$$

$$\beta = 124.95 \pm 0.01^\circ$$

The crystal was mounted along the  $(\bar{1}, 0, 4)$  axis with the b-axis at  $\text{Chi}=0$ . The crystal was then transferred to a General Electric XRD-490 automated diffractometer and a set of peak-height intensity data was collected using the stationary crystal-stationary counter method. Copper  $K\alpha$  radiation with balanced nickel and cobalt filters was utilized in the data collection.

A reflection was considered observed if:

$$(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 200 \text{ counts}$$

(15 second counting time)

The  $\sigma$ 's were based entirely on counting statistics. The 1895 reflections were measured out to a value of  $2\theta = 160^\circ$ . Of these, 1538 (81%) satisfied the above criterion and were considered observed. Intensities were corrected for

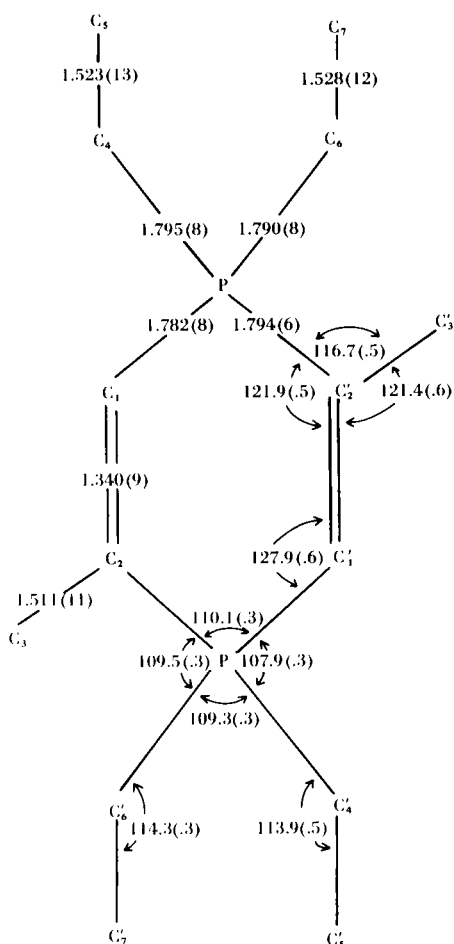


Figure 1 - Schematic View of Molecule. Bond Distances and bond angle indicated with estimated standard deviations in the last figures given in parentheses.

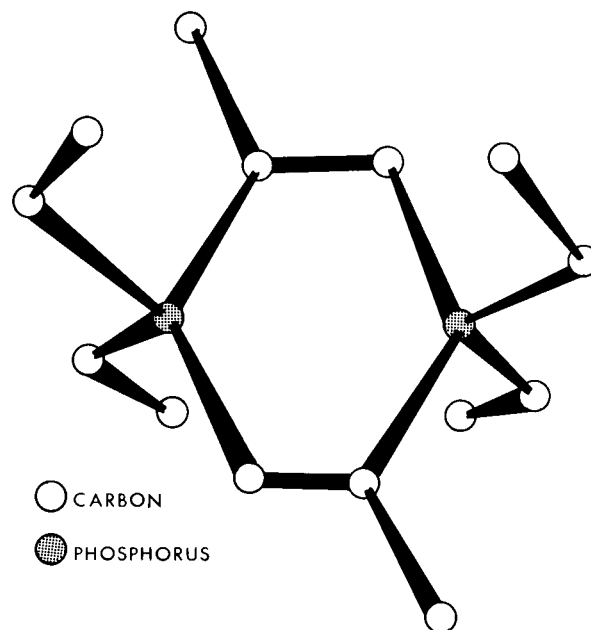


Figure 2 - Perspective View of the Molecule

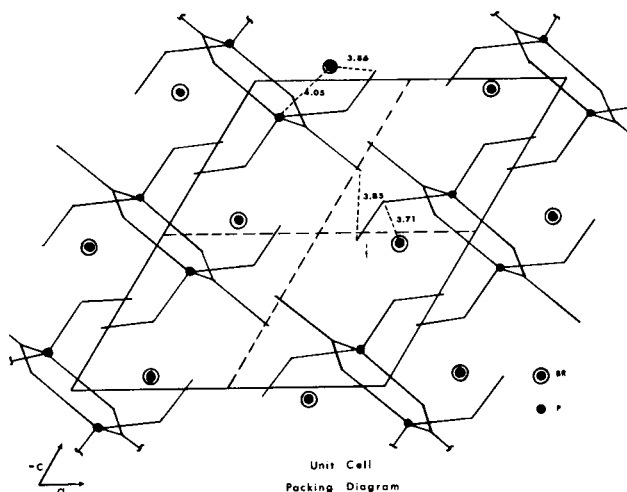


Figure 3 - Contents of the Unit Cell Projected Down the b-axis. Both bromine-carbon distances less than  $4.0 \text{ \AA}$  indicated. Shortest carbon-carbon distance and shortest bromine-phosphorus distance shown.

absorption as a function of  $\phi$  only, with a maximum difference of 11% over the entire  $\phi$  range. The intensities were also corrected for  $K\alpha_1 - K\alpha_2$  splitting and then converted to structure amplitudes in the usual fashion.

The model previously refined anisotropically to a value of  $R=0.16$ , based on film data, was used as a trial structure. A series of isotropic refinements reduced the reliability index ( $R$ ) to a value of  $0.14_8$ . After conversion

TABLE I  
Final Coordinates and Anisotropic Temperature Factors

Atom	Fractional Coordinates (Standard Deviations $\times 10^4$ in parentheses)			Anisotropic Thermal Parameters ( $\times 10^4$ ) (Standard Deviations ( $\times 10^4$ ) in parentheses)					
	X	Y	Z	$\beta(11)$	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
Br	1.2165 (1)	1.3197 (1)	0.4613 (1)	207 (2)	24 (1)	106 (1)	-12 (1)	51 (1)	-3 (1)
P	0.8581 (3)	1.0893 (1)	0.3820 (2)	90 (4)	12 (1)	49 (2)	6 (1)	18 (2)	2 (1)
C1	0.8621 (10)	0.9085 (4)	0.4447 (7)	149 (18)	16 (3)	79 (8)	-1 (5)	54 (10)	1 (4)
C2	0.7440 (10)	0.9769 (4)	0.3477 (6)	82 (15)	24 (3)	48 (7)	4 (5)	21 (8)	1 (3)
C3	0.5099 (11)	0.9623 (5)	0.2010 (8)	104 (17)	30 (3)	78 (9)	3 (6)	1 (10)	-3 (4)
C4	0.6845 (11)	1.1658 (4)	0.4044 (8)	155 (19)	24 (3)	86 (9)	18 (6)	30 (11)	2 (4)
C5	0.6579 (13)	1.1394 (6)	0.5326 (9)	213 (23)	45 (4)	126 (11)	12 (8)	107 (14)	-13 (6)
C6	0.8635 (11)	1.1248 (4)	0.2221 (8)	162 (19)	23 (3)	75 (8)	10 (6)	37 (10)	6 (4)
C7	1.0080 (15)	1.0650 (6)	0.1919 (9)	283 (27)	47 (4)	116 (11)	2 (9)	125 (15)	5 (6)

Anisotropic Thermal Parameters of the form.

$$\exp[-\beta(11)h^2 + \beta(22)k^2 + \beta(33)l^2 + 2\beta(12)hk + 2\beta(13)hl + 2\beta(23)kl]$$

TABLE II  
Calculated Hydrogen Coordinates

Atom (a)	X	Y	Z
H11	0.779	0.845	0.413
H14	0.756	1.231	0.427
H24	0.520	1.168	0.298
H16	0.696	1.126	0.122
H26	0.929	1.192	0.245

(a) The last digit refers to the carbon to which the hydrogen atom is bonded.

to anisotropic temperature factors, refinement was continued until all of the parameter shifts were less than one-tenth the estimated standard deviation for the same parameter. The data refined to a value of  $R=0.10_0$ . An extinction difficulty became apparent in the low order, high intensity data. Consequently, all reflections with  $2\theta < 20^\circ$  were omitted, the data was re-reduced, and a new list (1475 reflections) was compiled. A new series of isotropic refinements followed by anisotropic refinements led to a reliability index of  $R=0.06_2$ . At this stage a difference Fourier map was calculated. No peaks higher than  $0.6 \text{ e}^-/\text{\AA}^3$  were observed. The five highest peaks, ranging in height from  $0.4 \text{ e}^-/\text{\AA}^3$  to  $0.6 \text{ e}^-/\text{\AA}^3$  corresponded to positions calculated for the hydrogen atoms on carbons  $C_1$ ,  $C_4$  and  $C_6$ . In the regions where methyl hydrogens should have been observed (around carbons  $C_3$ ,  $C_5$  and  $C_7$ ), very diffuse positive regions of

heights ranging from  $0.1\text{-}0.3 \text{ e}^-/\text{\AA}^3$  were observed. It was thus decided to use the calculated positions for those five hydrogens where definite peaks were found in all further least squares refinement but to hold both their coordinates and temperature factors fixed and allow only the carbons to which they were attached to shift. It was further assumed that the remaining hydrogens not readily observed (all  $-\text{CH}_3$  type hydrogens) were undoubtedly disordered and so no further attempt would be made to include them in the calculations. Ten additional cycles of least-squares lowered the reliability index from  $0.06_2$  to  $0.05_9$ . The C-H distances originally assumed to be  $1.05\text{\AA}$  now ranged from  $1.04\text{-}1.06\text{\AA}$  and *all* shifts had become so negligibly small that the structure refinement was considered completed.

#### Results and Discussion.

The final coordinates and anisotropic temperature factors are given in Table I. The positions calculated for the five hydrogens included in the last set of refinements are given in Table II. Figure 1 shows the bond parameters of all atoms (excluding the bromine and the hydrogens) in a schematic fashion. A perspective view of the molecule is shown in Figure 2. The estimated standard deviations are  $0.00_8\text{\AA}$  in the P-C bonds; less than  $0.01_2\text{\AA}$  in the C-C bonds; and  $0.6^\circ$  or less in the angles involving these atoms. The precision as measured by the range of chemically (but not crystallographically) equivalent distances and angles agrees within the estimated standard deviations.

The P-C distances in the ring average to  $1.78_8 \pm 0.00_6\text{\AA}$ . The P-C distances (to the ethyl carbons) average to  $1.79_3$

TABLE III  
Best Planes Results  
(primes refer to centrosymmetric equivalents)

Plane	Atoms in Plane	Equation of Plane	Estimated Standard Deviation
1	P, C <sub>1</sub> , C <sub>2</sub> , P', C' <sub>1</sub> , C' <sub>2</sub>	.8274 p - .2141 q - .5191 r = -1.984	0.003 Å
2	P, C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> , P', C' <sub>1</sub> , C' <sub>2</sub> , C' <sub>3</sub>	.8341 p - .2124 q - .5091 r = -1.889	0.015 Å
3	P, C <sub>4</sub> , C <sub>5</sub> , C <sub>6</sub> , C <sub>7</sub>	.5439 p + .5545 q + .6299 r = 13.069	0.018 Å

## Dihedral Angles

Planes Involved	Dihedral Angle
Planes 1 and 3	89.8°
Planes 1 and 3'	89.9°

$\pm 0.00_3$  Å. Since these two values are statistically identical, a more realistic value to use would be the average of all four P-C distances ( $1.79_0 \pm 0.00_4$  Å). The angles about the phosphorus substantiate this equivalence, averaging  $109.5 \pm 0.5^\circ$ . The tetrahedral arrangement about the phosphorus and the P-C distances compare favorably to such an arrangement in the limited number of other compounds cited in the literature with an analogous P-C bond (9).

The C-C distances within the ring ( $1.34_0$  Å) make it clear that this is, in fact, a diene and not a delocalized ring system. The angles about the C<sub>2</sub> diene carbon ( $120.0 \pm 2.2^\circ$ ) further support this point of view.

The planarity of this six-membered ring, coupled with the very slight lengthening of the C=C distance of  $1.34_0$  Å (versus the usual 1.32 distance for a C-C double bond (10)), and the fact that the average P-C distances lie at the shorter end of the range of such known distances lend themselves to an interesting conjecture. Although these differences in distances are not statistically significant they suggest the possibility that the hexaphenyl substituted analogue may involve some such delocalization. Whether or not this is the case, must await the determination of that structure (Ia).

The values for the C-C single bonds (C<sub>2</sub>-C<sub>3</sub> =  $1.51_1$  Å, C<sub>4</sub>-C<sub>5</sub> =  $1.52_3$ , C<sub>6</sub>-C<sub>7</sub> =  $1.52_8$ ) are those to be expected. Similarly, the value of  $114.1 \pm 0.3^\circ$  for the angles in each of the ethyl groups agrees with other such values found in the literature (11).

Calculations of best planes fit show that the six-membered ring is planar with estimated standard deviations of  $0.00_3$  Å. If one calculates the best plane including the two ring methyl carbons, the eight atom plane has an estimated standard deviation of  $0.015$  Å. The four ethyl carbons on either side of the ring each lie in a

plane (E. S. D. =  $0.018$  Å) which has a dihedral angle of  $89.8^\circ$  with the six-membered ring. This data is summarized in Table III. Thus, the structure can be visualized as consisting of two perpendicular planes namely, the eight atom plane consisting of the six-membered ring and the two ring methyl carbons; and the eight atom plane containing the four ethyl carbons extended in a crab-like fashion over the plane of the six-membered ring.

The orientation of these ethyl carbon atoms over the ring is a relatively unusual feature which, to our knowledge, has not been seen in other simple ring systems. A partial explanation may involve the packing in the unit cell (illustrated in Figure 3) although no exceptionally short distances are apparent. A more reasonable explanation for this conformation (and the planarity of the six-membered ring) can be deduced from inspection of accurately made scale models of the molecule. If one twists the ethyl chains so that they no longer overlap the six-membered ring, the atoms at the tail-end (C<sub>5</sub> and C<sub>7</sub>) approach each other at a distance of 2.1 Å. Similarly, as one distorts the six-membered ring from planarity these same atoms rapidly approach each other. It thus seems reasonable to assume that the planar structure is, in fact, the conformation that the molecule would have, even if it were not in the crystal state.

## Acknowledgments.

The authors wish to thank Professor Adam Aguiar for samples of the compound. We also wish to acknowledge the partial financial support of a grant (GM-08348-09) from the National Institutes of Health in support of this and further studies. Finally, we wish to thank the Computation Center at L. S. U. N. O. for the use of the P. D. P.-10 computer facilities.

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Received June 4, 1970

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