

The Crystal and Molecular Structure of 1,1,2,4,4,5-Hexaphenyl-1,4-diphosphoniacyclohexadiene-2,5 Dibromide

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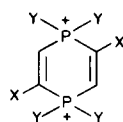
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The crystal and molecular structure of 1,1,2,4,4,5-hexaphenyl-1,4-diphosphoniacyclohexadiene-2,5 dibromide has been determined by a single crystal, x-ray diffraction study using diffractometer data. The compound crystallizes in the space group $P2_1/c$ with unit cell constants $a = 8.813(1)$, $b = 36.736(4)$, $c = 12.478(1)$ Å, and $\beta = 120.91^\circ(1)$. The structure was solved by the heavy atom method and refined by block-diagonal least-squares to a final $R = 0.04$ for the 2761 statistically significant reflections. The structure determination shows that the central phosphonium ring is a diene and not a delocalized structure as anticipated. The ring is in the boat conformation with the axial phenyl rings aligned essentially parallel to each other and 3.55 Å apart.

Introduction.

There has been some controversy (1,2) about the existence and nature of π -electron delocalization in phosphonitrilic systems. Previous systems designed to explore this possibility have proven rather unstable (3,4). A less suitable example (5) was investigated (1a) and although shown to be a diene was sufficiently ambiguous to allow for the possibility that the hexaphenyl substituted derivative (1b) reported herein was indeed an example of such a delocalized system.



- I
 (a) $X = C_2H_5$, $Y = C_6H_5$
 (b) $X = Y = C_6H_5$

Further support for this conjecture was supplied by the nmr spectrum of this compound reported. The ^{31}P nmr shifts measured at 40.5 Mc/sec (shifts expressed in parts per million of methanol solution relative to an external standard of 85% H_3PO_4) were +3.5 cps (6). Previously, in simple phosphonium salts one encountered large negative shifts (-20 to -30 cps) rather than any positive shift. For these reasons, the structure of the dibromide salt of the hexaphenyl substituted derivative (1b) was determined and is herein reported.

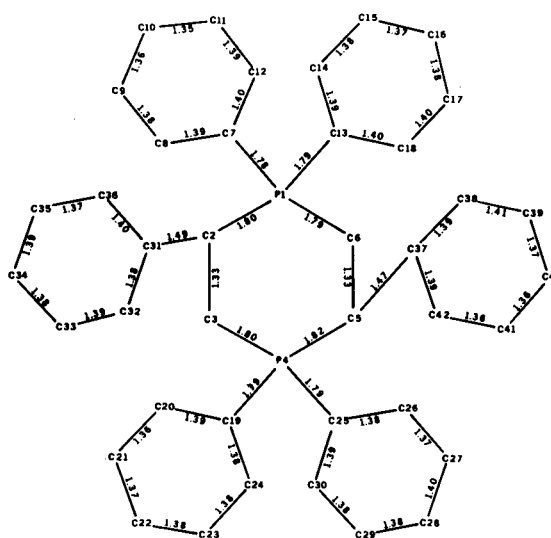


Figure 1. Schematic drawing of the molecule with bond distances indicated.

EXPERIMENTAL

A sample of the title compound ($C_{40}H_{32}P_2Br_2 \cdot H_2O$) (kindly furnished to us by Professor Adam Aquiar of Tulane University) (7) was recrystallized by a solvent exchange technique (8) using acetonitrile and diethyl ether. A single crystal (.23 x .12 x .09 mm) was mounted with (h00) coincident with the phi axis of a General Electric XRD-5 diffractometer. The reciprocal lattice showed only $P2_1/m$ symmetry characterizing the crystal as monoclinic. Extinctions when l was odd for the $(h0l)$ reflections and k odd for the $(0k0)$ reflections uniquely determined the space

TABLE I
 Fractional Coordinates and Anisotropic Thermal Parameters (a)
 (Standard Deviations $\times 10^4$ in parentheses)

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
BR1	0.3679(1)	0.1386(0)	0.0666(1)	181(2)	8(0)	58(1)	0(0)	26(1)	4(0)
BR2	0.2288(1)	0.3746(0)	0.0735(1)	149(2)	8(0)	115(1)	5(0)	91(1)	5(0)
P1	0.6227(3)	0.0869(0)	0.4012(2)	75(4)	1(0)	57(2)	1(1)	38(2)	1(0)
P4	0.5905(2)	0.1733(0)	0.4279(2)	62(4)	1(0)	43(2)	0(1)	25(2)	0(0)
C2	0.4134(9)	0.1070(2)	0.3596(7)	80(15)	2(1)	50(7)	0(2)	39(9)	1(2)
C3	0.4065(9)	0.1427(2)	0.3754(6)	78(14)	2(1)	43(7)	-1(2)	23(8)	-2(2)
C5	0.7267(9)	0.1557(2)	0.3688(7)	62(14)	2(1)	49(7)	1(2)	29(8)	1(2)
C6	0.7391(10)	0.1197(2)	0.3642(7)	99(15)	3(1)	47(7)	6(2)	38(8)	2(2)
C7	0.5916(11)	0.0464(2)	0.3141(7)	136(18)	2(1)	78(9)	0(2)	73(10)	1(2)
C8	0.4834(13)	0.0469(2)	0.1854(8)	207(23)	6(1)	67(9)	7(3)	61(12)	0(2)
C9	0.4515(15)	0.0150(3)	0.1183(9)	283(28)	7(1)	90(11)	-1(4)	91(15)	-8(3)
C10	0.5271(14)	-0.0167(2)	0.1780(10)	242(25)	4(1)	128(13)	-8(3)	113(15)	-10(3)
C11	0.6330(15)	-0.0177(2)	0.3037(11)	329(30)	2(1)	173(15)	1(3)	173(19)	0(2)
C12	0.6704(12)	0.0137(2)	0.3752(8)	161(20)	3(1)	89(10)	2(3)	59(12)	2(2)
C13	0.7467(10)	0.0784(2)	0.5654(7)	81(15)	2(1)	66(8)	1(2)	35(9)	0(2)
C14	0.9286(11)	0.0730(2)	0.6230(8)	107(16)	3(1)	81(9)	3(3)	50(10)	3(2)
C15	1.0298(11)	0.0683(2)	0.7509(9)	111(18)	5(1)	106(11)	6(3)	44(12)	2(2)
C16	0.9509(12)	0.0686(3)	0.8207(8)	179(21)	7(1)	52(8)	0(3)	27(11)	3(2)
C17	0.7709(13)	0.0739(3)	0.7659(8)	192(22)	8(1)	66(9)	3(4)	70(12)	2(2)
C18	0.6659(10)	0.0791(2)	0.6369(8)	88(16)	5(1)	67(8)	0(3)	42(9)	1(2)
C19	0.5040(9)	0.2177(2)	0.3689(7)	64(14)	3(1)	58(8)	3(2)	35(9)	2(2)
C20	0.4173(11)	0.2242(2)	0.2408(8)	116(17)	4(1)	63(8)	0(3)	33(10)	0(2)
C21	0.3533(11)	0.2582(2)	0.1986(8)	115(17)	6(1)	72(9)	4(3)	30(10)	9(2)
C22	0.3649(12)	0.2857(2)	0.2753(10)	146(20)	3(1)	140(12)	9(3)	88(13)	12(2)
C23	0.4495(12)	0.2791(2)	0.4016(9)	173(21)	2(1)	133(12)	2(3)	97(13)	0(2)
C24	0.5205(11)	0.2453(2)	0.4493(8)	136(18)	4(1)	87(9)	0(3)	62(11)	-2(2)
C25	0.7202(10)	0.1727(2)	0.5952(7)	83(14)	2(1)	56(7)	1(2)	31(9)	0(2)
C26	0.6350(11)	0.1748(2)	0.6620(7)	118(17)	5(1)	60(8)	4(3)	53(10)	0(2)
C27	0.7315(12)	0.1720(3)	0.7898(8)	148(19)	8(1)	64(9)	2(3)	65(11)	0(2)
C28	0.9145(12)	0.1672(2)	0.8493(7)	161(20)	6(1)	42(8)	-1(3)	34(10)	-4(2)
C29	0.9982(10)	0.1650(2)	0.7820(8)	93(16)	4(1)	64(8)	2(3)	26(10)	2(2)
C30	0.9014(10)	0.1679(2)	0.6533(7)	105(16)	4(1)	47(7)	1(3)	37(9)	0(2)
C31	0.2494(10)	0.0847(2)	0.3031(7)	109(16)	1(1)	59(7)	-4(2)	48(9)	-3(2)
C32	0.0972(11)	0.0981(2)	0.2016(8)	106(17)	5(1)	71(9)	-2(3)	29(10)	-1(2)
C33	-0.0598(11)	0.0784(3)	0.1472(9)	85(17)	10(1)	80(10)	-7(3)	5(11)	-11(3)
C34	-0.0622(14)	0.0448(3)	0.1963(10)	184(24)	9(1)	126(13)	-26(4)	70(15)	-13(3)
C35	0.0910(13)	0.0309(3)	0.2968(10)	179(23)	7(1)	114(12)	-18(4)	40(14)	3(3)
C36	0.2454(12)	0.0502(2)	0.3487(9)	167(21)	4(1)	96(10)	-11(3)	54(12)	0(2)
C37	0.8175(10)	0.1813(2)	0.3296(7)	73(15)	4(1)	62(8)	3(2)	39(9)	5(2)
C38	0.8279(12)	0.1728(2)	0.2254(9)	180(21)	5(1)	105(10)	2(3)	101(13)	6(2)
C39	0.9148(15)	0.1966(3)	0.1858(10)	308(30)	10(1)	143(14)	17(5)	177(18)	17(3)

Table I (Continued)

C40	0.9885(13)	0.2282(3)	0.2509(10)	162(22)	7(1)	154(14)	-4(3)	94(15)	12(3)
C41	0.9785(12)	0.2363(2)	0.3538(9)	120(19)	4(1)	134(12)	-5(3)	50(13)	10(2)
C42	0.8930(11)	0.2137(2)	0.3919(8)	93(17)	4(1)	91(10)	-1(3)	39(10)	2(2)
OX	0.5083(11)	0.3925(2)	0.3829(7)	284(20)	12(1)	143(10)	-20(3)	107(12)	-6(2)

(a) Anisotropic temperature factors of the form:

$$\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$$

group as P2₁/c. The final structure determination reconfirmed this assignment. Lattice constants were determined by a least-squares fit of 54 carefully measured two-theta values of the Cu-K α_1 and Cu-K α_2 doublet for $2\theta > 70^\circ$ under fine conditions (1° take-off angle and $.05^\circ$ slit). The resultant lattice constants and their estimated standard deviations are:

$$\begin{aligned} a &= 8.813 \pm 0.001 \text{ \AA} \\ b &= 36.736 \pm 0.004 \text{ \AA} \\ c &= 12.478 \pm 0.001 \text{ \AA} \\ d &= 120.91^\circ \pm 0.01 \end{aligned}$$

The calculated density of 1.41 g/cc, assuming four formula weights per unit cell, agrees well with the experimental density of 1.40 \pm .02 g/cc (by flotation methods).

Intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-crystal, stationary-counter method using balanced nickel and cobalt filters and Copper K α radiation. A total of 6358 independent reflections were measured to a two-theta maximum of 140° ($d = .820$) in two shells, $0-100^\circ$ (5 second counting time) and $100-140^\circ$ (10 second counting time). The intensities of the two shells were put on a common scale and a total of 2761 (43%) were considered observed by the criteria, $(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 70$ counts where the σ 's were based entirely on counting statistics. The intensities were corrected for Lorentz-polarization and K α_1 -K α_2 splitting in the usual manner, and for absorption as a function of phi only with a maximum difference of 27% over the entire range of phi (linear absorption coefficient with Cu radiation is 43.8 cm^{-1}).

Structure Determination.

The coordinates of the two bromine atoms were located from a three dimensional Patterson function and used in the phasing of a subsequent electron density map. The two phosphorus atoms were readily evident on this map. Although a number of smaller peaks were also apparent, only the bromines and phosphorus atoms were included in our refinement at this stage. The bromine and phosphorus atom coordinates and isotropic temperature factors were refined by block-diagonal least-squares (9) using unit weights to a value of $R = .33$. A second electron density map phased by the refined bromine and phosphorus coordinates was calculated and showed all other non-hydrogen atoms including one peak approximately the same size as a carbon atom unattached to the primary molecule. This peak was assigned as the oxygen of a water molecule. The coordinates and isotropic temperature factors of all 45 non-hydrogen atoms were refined by block-diagonal least-squares to $R = .09$. The isotropic temperature factors then were converted to anisotropic temperature factors, the refinement continued until convergence at $R = .05$, and a difference electron density map calculated to locate the hydrogen atoms. Positive regions of electron density were found at the

TABLE II
Calculated Hydrogen Coordinates

Atom	X	Y	Z
H3	0.289	0.153	0.356
H6	0.821	0.110	0.336
H8	0.427	0.071	0.140
H9	0.372	0.015	0.023
H10	0.501	-0.040	0.127
H11	0.687	-0.042	0.347
H12	0.752	0.013	0.471
H14	0.987	0.073	0.571
H15	1.163	0.065	0.793
H16	1.026	0.065	0.915
H17	0.715	0.074	0.820
H18	0.533	0.083	0.595
H20	0.405	0.204	0.181
H21	0.294	0.263	0.104
H22	0.311	0.310	0.240
H23	0.462	0.299	0.461
H24	0.584	0.241	0.544
H26	0.501	0.178	0.616
H27	0.671	0.173	0.841
H28	0.989	0.165	0.944
H29	1.131	0.161	0.827
H30	0.962	0.166	0.602
H32	0.099	0.123	0.167
H33	-0.171	0.088	0.070
H34	-0.178	0.031	0.159
H35	0.089	0.006	0.332
H36	0.359	0.039	0.421
H38	0.772	0.149	0.176
H39	0.923	0.190	0.109
H40	1.053	0.246	0.223
H41	1.033	0.260	0.402
H42	0.884	0.221	0.468

expected hydrogen positions but were rather diffuse. Therefore, the coordinates of the 32 hydrogen atoms (excluding those of the water molecule) were calculated based upon the expected geometry (120° angles and 1.03 \AA C-H bond length). Refinement was continued varying only the coordinates and anisotropic temperature factors of the non-hydrogen atoms until the shifts were less than one-tenth their estimated standard deviation. The final value of the reliability index was $R = 0.04$ and the structure determination was assumed to be completed.

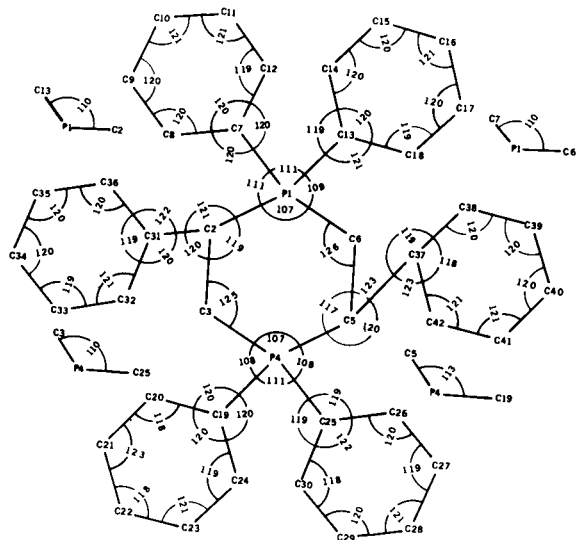


Figure 2. Schematic drawing of the molecule with bond angles indicated.

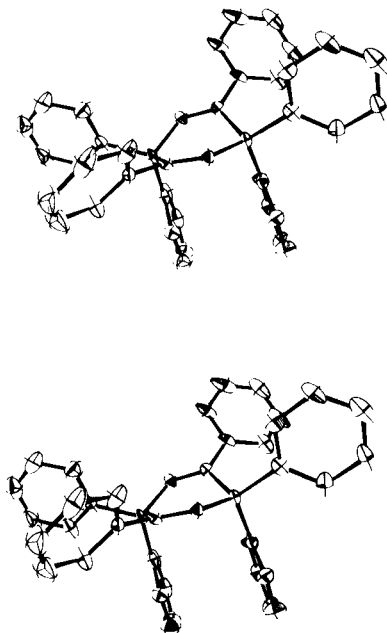


Figure 3. ORTEP stereodrawing of the molecule.

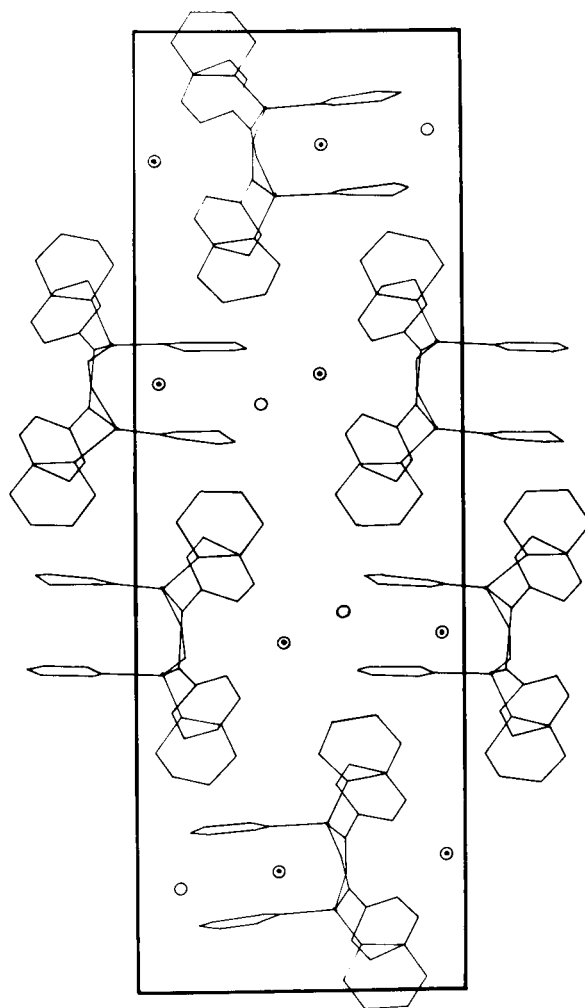


Figure 4. Contents of the unit cell projected down the (100) axis. The b-axis is the long axis.

⊗ Bromine

○ Oxygen of water molecule

Results and Discussion.

Table I lists the final refined coordinates and anisotropic temperature factors for all of the non-hydrogen atoms together with their estimated standard deviation (ESD). The calculated positions of the fixed hydrogen atoms included in the final cycles of refinement (with fixed isotropic temperature factors of $\beta = 4.0 \text{ \AA}^2$) are given in Table II.

The six crystallographically independent phenyl rings serve as useful indicators of the reliability of the molecular parameters. The C-C distances and the CCC internal angles averaged over all of the rings are 1.385 \AA and 120.0° , respectively, with average deviations of $.01 \text{ \AA}$ in the distances and 1.0° in the angles. If one considers

averages of each ring independently, the C—C average distances range from 1.38₀ to 1.39₅ Å while the CCC internal angles average to 120° for each ring. A further measure of the reliability of the determination is obtained from the least-squares fit of the planarity of these rings. Calculations show that all six of the phenyl rings are planar with ESD values ranging from .002-.009 Å.

The P—C distances average to 1.79₅ ± .005 Å for all eight distances in agreement with the value of 1.79₀ ± .004 Å previously reported (5) for an analogous structure in which the diphosphonium ring was planar. The C—C double bond distance of 1.33₀ Å, confirming the diene nature of this ring, also closely parallels the value of 1.34₀ found previously (5). The internal angles at each of the phenyl substituted diene carbon atoms (118 ± 1°) and at the unsubstituted diene carbon atoms (125 ± 1°) support the assumed sp² hybridization. Calculations of best planes fit using the four diene carbon atoms as the central plane (ESD = .03) and each phosphorus and its adjacent carbons as secondary planes readily show the boat conformation of this central ring. Dihedral angles between these planes of 151° and 152° are observed.

Figures 1 and 2 show schematic drawings of the molecule with the bond distances and bond angles, respectively, indicated on the two figures. Figure 3 gives an ORTEP stereo view of the molecule in which its actual conformation is evident.

The question of delocalization of the four π-electrons over the phosphorus atom (6) was partially answered in an earlier structure study (5) although not in a definitive manner. However, if such delocalization did exist in these diphosphoniacyclohexadiene systems, it should be most apparent in the hexaphenyl derivative, namely, this compound. The fact that it does not occur here is evident from the boat conformation of the ring, the normal C—C double bond distance (1.33 Å) and the normal P—C distances (1.79₅ ± .005 Å) indicating that such delocalization does not occur in any of these systems. Thus, the unusual nmr shifts observed should be interpreted as indicative of substituent conformational alignment and not as a function of delocalization of the π-electronic charge within

the ring. The alignment of the two axial phenyl rings parallel to each other and approximately 3.55 Å apart may in large part explain these shifts.

Figure 4 shows the packing within the unit cell. There are five somewhat short Br-light atom contacts. The shortest two (3.32, 3.41 Å) involve the packing of the water of hydration and the other three involve Br—C distances (3.50, 3.52, 3.53 Å). None of these are sufficiently close to merit additional discussion nor is it felt they would affect the geometry of the system. There is only one contact distance between light atoms less than 3.50 Å and this distance involves a carbon and the oxygen from the hydrated water (3.40 Å). Consequently, there should be no appreciable distortion of the molecule because of packing effects in the solid.

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