

# The Crystal and Molecular Structure of 1,1,4,4-Tetraphenyl-1,4-diphosphoniacyclohexane Dibromide

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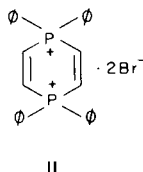
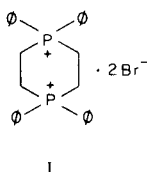
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The crystal and molecular structure of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide has been determined by a single-crystal, x-ray diffraction study using diffractometer data. The compound crystallizes in the monoclinic space group  $P2_1/c$  with unit cell constants of  $a = 12.777(1)$ ,  $b = 26.180(2)$ ,  $c = 16.283(1)$  Å, and  $\beta = 91.18(1)^\circ$ . The structure was solved by the heavy atom method with the 4176 independent and statistically significant structure factors refining to a value of  $R = 0.07$ . The diphosphonium ring is in the chair conformation with each phosphorus ion having an axial and equatorial phenyl ring attached. P-C and C-C bond lengths of  $1.78 \pm .03$  Å and  $1.53 \pm .03$  Å respectively agree well with the literature value for these distances.

## Introduction.

The title compound (I) was first prepared and characterized chemically in 1966 (1). In a later attempt to synthesize the analogous diphosphoniacyclohexadiene (II) (2) by an alternate route, the title compound (I) was



obtained instead. In attempting to rationalize the synthetic difficulties, it was postulated that the structure of the tetraphenyl saturated ring system might very well have an unexpected geometry which could account for its preferential formation by the alternate route. Consequently, a structure determination was undertaken of (I) and is reported herein.

## EXPERIMENTAL

A sample of the title compound ( $C_{28}H_{28}P_2Br_2 \cdot H_2O$ ) was kindly supplied to us by Professor Adam Aguiar (3) of Tulane University. A single crystal, recrystallized from acetonitrile and mounted on a General Electric XRD-5, showed monoclinic symmetry with extinctions for the  $(h0l)$  reflections when  $l$  was odd and for the  $(0k0)$  reflections when  $k$  was odd which uniquely identified the space group as  $P2_1/c$ . Lattice constants were determined by a least-squares fit of 54 carefully measured ( $1^\circ$  takeoff angle and  $.05^\circ$  slit) two-theta values of the  $Cu K\alpha_1-K\alpha_2$  doublet at two-theta values greater than  $70^\circ$ . The resultant lattice constants and their estimated standard deviations (ESD) are:

$$a = 12.777 \pm 0.001 \text{ \AA}$$

$$b = 26.180 \pm 0.002 \text{ \AA}$$

$$c = 16.238 \pm 0.001 \text{ \AA}$$

$$\beta = 91.18 \pm 0.01^\circ$$

The calculated density of 1.47 gms/cc for eight molecules per unit cell is in agreement with the experimental density of  $1.47 \pm .01$  gms/cc measured by flotation techniques.

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  $Cu-K\alpha$  radiation. Three crystals, all measuring less than 0.25 mm in their largest dimension, were used to collect a total of 8641 reflections to  $2\theta_{max} = 120^\circ$  ( $d = 0.89$  Å) of which 4176 were considered observed based on counting statistics. The intensities were corrected in the usual manner for Lorentz-polarization effects and for  $K\alpha_1-K\alpha_2$  splitting. Since the linear absorption coefficient is only  $54.0 \text{ cm}^{-1}$ , absorption was corrected as a function of  $\phi$  only.

## Structure Determination.

Since there are eight molecules in the unit cell, two unique crystallographic molecules must be determined. The three-dimensional Patterson map did not lead to unambiguous positions for the four bromines and four phosphorus atoms which needed to be determined. In fact, an initial trial structure refined to a value of  $R = 0.22$  before it was realized that the determination had reached a false minimum. A re-interpretation of the Patterson map led to the correct locations of two of the four bromines. An electron density map phased by these two bromines revealed the remaining two bromines, the four phosphorus atoms and a number of smeared out smaller peaks. Isotropic refinement of the four bromines and four phosphorus atoms using block-diagonal least-squares (4) led to a value of  $R = 0.25$ . A second electron density map phased by these eight heavier atoms revealed all of the lighter atoms in both molecules and the oxygen atom of the water of crystallization. Isotropic refinement of all 65 non-hydrogen atoms led to a value of  $R = 0.10$  using unit weights. After conversion to anisotropic temperature factors and a change to  $\frac{1}{\sigma^2}$  weights, refinement was continued and led to a value of  $R =$

TABLE I

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

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
BR1	0.0948( 2)	0.1929( 1)	0.0237( 1)	37( 1)	10(0)	28( 1)	-2( 1)	3( 1)	4(0)
BR2	0.4370( 2)	0.0586( 1)	0.1177( 2)	55( 2)	10(0)	47( 1)	-3( 1)	6( 1)	0(1)
BR3	0.5473( 2)	0.0481( 1)	0.3974( 1)	59( 2)	11(0)	38( 1)	5( 1)	17( 1)	1(1)
BR4	0.9391( 2)	0.3211( 1)	0.2289( 1)	56( 2)	16(0)	27( 1)	-14( 1)	7( 1)	0(1)
P1	0.8379( 4)	0.0980( 2)	0.1340( 3)	13( 3)	7(1)	13( 2)	-2( 1)	1( 2)	0(1)
P4	0.7101( 4)	0.1841( 2)	0.2466( 3)	24( 3)	6(1)	11( 2)	-4( 1)	3( 2)	0(1)
P31	0.3093( 4)	0.3310( 2)	0.0091( 3)	19( 3)	7(1)	12( 2)	0( 1)	1( 2)	0(1)
P34	0.1896( 4)	0.4224( 2)	0.1183( 3)	18( 3)	6(1)	13( 2)	-1( 2)	0( 2)	0(1)
C2	0.7456(13)	0.0830( 6)	0.2077(10)	25(12)	3(2)	18( 8)	1( 4)	1( 8)	-3(4)
C3	0.6577(13)	0.1204( 5)	0.2199(10)	34(13)	-2(2)	26( 8)	-6( 4)	4( 8)	-2(3)
C5	0.8046(14)	0.1995( 6)	0.1718( 9)	59(15)	3(2)	11( 7)	-26( 5)	-10( 8)	2(4)
C6	0.8892(12)	0.1555( 4)	0.1647(10)	18(11)	-5(2)	35( 9)	0( 3)	5( 8)	1(3)
C7	0.9419(13)	0.0524( 5)	0.1317(10)	22(11)	2(2)	25( 8)	-14( 5)	4( 8)	0(4)
C8	0.9167(17)	-0.0000( 9)	0.1334(14)	39(18)	18(4)	52(13)	-4( 7)	10(13)	6(7)
C9	0.9949(18)	-0.0361( 8)	0.1243(15)	70(22)	10(4)	82(16)	26( 7)	30(15)	1(7)
C10	1.0971(16)	-0.0206( 5)	0.1173(14)	74(20)	-7(2)	98(16)	11( 5)	16(15)	0(5)
C11	1.1215(15)	0.0294( 9)	0.1131(13)	17(14)	24(5)	49(13)	16( 7)	-3(11)	-2(7)
C12	1.0431(17)	0.0660( 7)	0.1225(14)	51(18)	11(4)	59(14)	-26( 7)	-6(13)	5(6)
C13	0.7729(14)	0.1038( 6)	0.0382(10)	45(14)	5(3)	15( 7)	28( 5)	-8( 8)	-3(4)
C14	0.6873(15)	0.0717( 7)	0.0195(11)	22(13)	15(4)	26( 9)	5( 6)	-5( 9)	-5(5)
C15	0.6348(16)	0.0746( 6)	-0.0560(12)	63(19)	5(3)	41(11)	-21( 6)	-6(12)	0(5)
C16	0.6772(17)	0.1063( 8)	-0.1157(12)	58(19)	15(4)	23( 9)	8( 8)	-10(11)	-9(5)
C17	0.7605(17)	0.1420( 6)	-0.0993(11)	101(22)	2(2)	30(10)	29( 6)	10(12)	-1(4)
C18	0.8120(15)	0.1355( 8)	-0.0224(11)	37(15)	21(5)	10( 8)	7( 7)	1( 9)	0(5)
C19	0.7713(12)	0.1822( 7)	0.3468(10)	0(10)	14(3)	20( 8)	1( 5)	0( 7)	-5(4)
C20	0.7341(15)	0.1509( 7)	0.4084(12)	31(15)	12(4)	31(10)	-4( 6)	0(10)	2(5)
C21	0.7756(19)	0.1512(10)	0.4874(12)	74(22)	36(7)	10( 9)	5(11)	-11(12)	8(6)
C22	0.8548(16)	0.1848(10)	0.5050(12)	56(18)	38(7)	23(10)	43(10)	-24(11)	-19(7)
C23	0.8904(18)	0.2204( 9)	0.4433(14)	57(20)	30(6)	40(12)	-2(10)	-20(13)	-22(7)
C24	0.8493(15)	0.2179( 8)	0.3672(11)	39(15)	14(4)	20( 9)	7( 6)	-11( 9)	-5(5)
C25	0.6084(14)	0.2306( 7)	0.2439(10)	26(13)	11(3)	9( 7)	8( 5)	-7( 8)	-4(4)
C26	0.6286(16)	0.2800( 6)	0.2191(13)	42(16)	2(2)	62(13)	4( 5)	-8(12)	-6(5)
C27	0.5511(18)	0.3182( 9)	0.2230(13)	59(19)	21(5)	32(11)	5( 9)	-19(12)	-2(6)
C28	0.4535(16)	0.3044( 8)	0.2510(13)	47(17)	12(4)	49(12)	15( 7)	-1(12)	-8(6)
C29	0.4320(16)	0.2547( 8)	0.2761(15)	32(16)	18(5)	69(15)	22( 7)	4(13)	-3(7)
C30	0.5101(17)	0.2185( 7)	0.2714(13)	59(19)	5(3)	54(13)	8( 6)	9(13)	4(5)
C32	0.2044(13)	0.3189( 5)	0.0806(10)	42(14)	-2(2)	28( 8)	-7( 4)	9( 9)	1(3)
C33	0.1300(15)	0.3630( 7)	0.0863(10)	39(15)	9(3)	12( 7)	9( 6)	3( 8)	0(4)
C35	0.2885(14)	0.4329( 6)	0.0461(10)	30(13)	4(3)	20( 8)	-5( 5)	-10( 8)	0(4)
C36	0.3655(14)	0.3895( 6)	0.0392(10)	50(15)	2(2)	18( 8)	16( 5)	8( 9)	1(4)
C37	0.4037(13)	0.2795( 7)	0.0156(10)	17(12)	12(3)	11( 7)	4( 5)	-7( 7)	-1(4)
C38	0.3745(14)	0.2330( 6)	0.0384(13)	30(14)	3(3)	67(13)	-17( 5)	1(11)	7(5)
C39	0.4436(17)	0.1923( 8)	0.0367(13)	65(20)	11(4)	53(13)	0( 7)	2(13)	0(6)

TABLE I (continued)

Atom	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C40	0.5432(18)	0.2021( 8)	0.0165(12)	78(21)	11(4)	38(11)	17( 8)	-8(13)	-5(5)
C41	0.5743(16)	0.2509( 8)	-0.0057(14)	35(16)	14(4)	62(14)	-1( 7)	17(12)	3(6)
C42	0.5061(16)	0.2909( 6)	-0.0050(13)	37(15)	4(3)	52(12)	0( 5)	10(11)	3(5)
C43	0.2569(13)	0.3362( 7)	-0.0939(10)	20(12)	13(3)	14( 8)	18( 5)	3( 8)	0(4)
C44	0.2998(14)	0.3672( 7)	-0.1516(10)	35(15)	13(4)	16( 8)	16( 6)	6( 9)	0(4)
C45	0.2657(17)	0.3641( 8)	-0.2288(12)	50(18)	22(5)	19( 9)	6( 8)	8(10)	3(6)
C46	0.1866(18)	0.3307(10)	-0.2529(12)	61(20)	36(7)	14( 9)	19(10)	-14(11)	7(7)
C47	0.1456(16)	0.2957( 8)	-0.1975(12)	38(15)	18(4)	37(11)	22( 7)	-16(11)	-10(6)
C48	0.1814(14)	0.2996( 7)	-0.1168(11)	28(13)	13(3)	22( 8)	0( 6)	0( 9)	0(5)
C49	0.0916(13)	0.4695( 5)	0.1183(10)	31(13)	-4(2)	33( 9)	-10( 4)	1( 9)	2(3)
C50	-0.0050(16)	0.4597( 8)	0.1483(13)	44(17)	13(4)	45(12)	2( 7)	1(12)	7(6)
C51	-0.0761(18)	0.5008( 8)	0.1552(14)	59(20)	12(4)	67(15)	21( 7)	11(14)	11(6)
C52	-0.0522(18)	0.5485( 9)	0.1333(13)	70(21)	22(5)	36(11)	24( 9)	-9(13)	-4(7)
C53	0.0459(17)	0.5602( 7)	0.0995(14)	66(20)	11(4)	71(15)	37( 8)	-11(14)	2(6)
C54	0.1158(16)	0.5199( 9)	0.0939(13)	30(16)	24(5)	33(11)	-2( 8)	-8(11)	-7(6)
C55	0.2499(14)	0.4149( 6)	0.2180(10)	31(14)	8(3)	18( 8)	21( 5)	-8( 8)	-4(4)
C56	0.2036(15)	0.3849( 8)	0.2779(11)	24(14)	22(5)	15( 8)	7( 7)	-1( 9)	-1(5)
C57	0.2448(17)	0.3833( 9)	0.3553(11)	55(19)	25(5)	14( 9)	1( 8)	-2(10)	8(6)
C58	0.3304(16)	0.4120( 8)	0.3789(11)	49(18)	23(5)	16( 9)	23( 8)	-13(10)	-3(5)
C59	0.3759(16)	0.4443( 9)	0.3191(12)	34(15)	25(5)	22(10)	3( 8)	-18(10)	-3(6)
C60	0.3351(14)	0.4457( 7)	0.2405(11)	32(14)	8(3)	22( 8)	10( 6)	1( 9)	0(4)
OXY	0.3551(15)	-0.0049( 7)	0.2789(11)	114(22)	36(5)	67(12)	-25( 9)	-20(13)	10(6)

(a) Anisotropic temperature factors of the form:

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

0.075. Hydrogen positions were calculated based on the expected geometry and included in the structure factor calculation leading to a final value of  $R = 0.07$ . All shifts in coordinates and temperature factors were less than one tenth the estimated standard deviations of their respective parameters and so refinement was assumed complete.

#### Results and Discussion.

Table I lists the final coordinates and anisotropic temperature factors for the refined non-hydrogen atoms. Estimated standard deviations (ESD) in the last place are given in parentheses. Table II lists the assumed hydrogen coordinates. An isotropic temperature factor of  $4.0 \text{ \AA}^2$  was arbitrarily assigned to each hydrogen atom in the final structure factor calculation.

The ESD values are  $1.78 \pm .02 \text{ \AA}$  for the P-C bonds and  $1.53 \pm .03$  for the C-C distances. All of the angles have ESD values of  $1^\circ$  or less. The average deviation of equivalent distances and angles contained in both molecules are equal to the ESD values. Consequently, a discussion of an "average" molecule and the average deviations in its parameters has no loss in generality.

TABLE II

Calculated Hydrogen Coordinates

Atom	X	Y	Z
H2'	0.782	0.077	0.264
H2''	0.711	0.048	0.193
H3'	0.610	0.110	0.266
H3''	0.615	0.124	0.168
H5'	0.838	0.234	0.186
H5''	0.768	0.204	0.116
H6'	0.926	0.155	0.221
H6''	0.944	0.170	0.125
H8	0.840	-0.011	0.141
H9	0.978	-0.073	0.127
H10	1.155	-0.047	0.116
H11	1.198	0.042	0.105
H12	1.060	0.105	0.121
H14	0.662	0.048	0.061

TABLE II (continued)

Atom	X	Y	Z
H15	0.576	0.053	-0.072
H16	0.644	0.108	-0.174
H17	0.814	0.140	-0.144
H18	0.877	0.158	-0.010
H20	0.675	0.126	0.392
H21	0.751	0.126	0.530
H22	0.887	0.187	0.561
H23	0.950	0.246	0.460
H24	0.875	0.242	0.323
H26	0.700	0.289	0.199
H27	0.563	0.353	0.203
H28	0.395	0.330	0.255
H29	0.361	0.245	0.296
H30	0.495	0.182	0.291
H32'	0.238	0.314	0.138
H32''	0.168	0.287	0.065
H33'	0.072	0.354	0.125
H33''	0.095	0.368	0.029
H35'	0.328	0.467	0.061
H35''	0.255	0.441	-0.011
H36'	0.404	0.387	0.094
H36''	0.422	0.400	-0.003
H38	0.299	0.227	0.054
H39	0.422	0.158	0.053
H40	0.598	0.173	0.015
H41	0.652	0.257	-0.021
H42	0.531	0.326	-0.020
H44	0.355	0.392	-0.135
H45	0.296	0.387	-0.274
H46	0.163	0.328	-0.314
H47	0.090	0.270	-0.216
H48	0.149	0.275	-0.074
H50	-0.025	0.425	0.163
H51	-0.148	0.495	0.178
H52	-0.105	0.578	0.134
H53	0.065	0.596	0.082
H54	0.189	0.529	0.073
H56	0.137	0.364	0.262
H57	0.212	0.359	0.396
H58	0.359	0.410	0.437
H59	0.436	0.467	0.337
H60	0.368	0.468	0.198

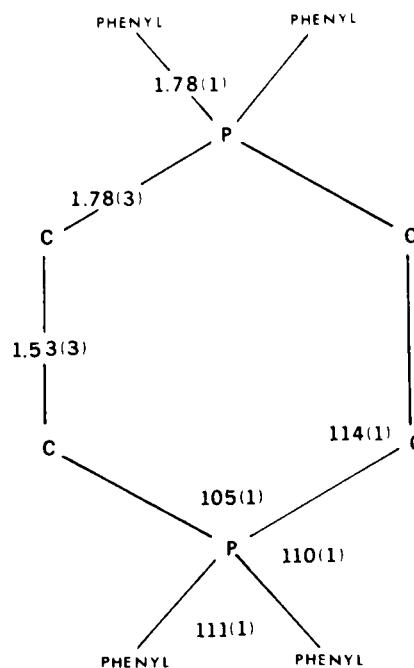


Figure 1 - Schematic drawing of central ring showing the averaged bond distances and angles together with the average deviation for each of these parameters.

Figure 1 shows a sketch of the central ring with the average value of each parameter together with the error obtained by averaging all such chemically equivalent values in both molecules. The four carbon atoms in the diposponium ring of each molecule are essentially planar as calculated by a least-squares fit to the best plane (ESD values of 0.011 and 0.002 Å for each of these planes). This central ring is in the chair conformation with dihedral angles of  $132 \pm 1^\circ$  as shown in Figure 2. Each phosphorus ion has two phenyl groups attached, one of which is equatorial and the other axial.

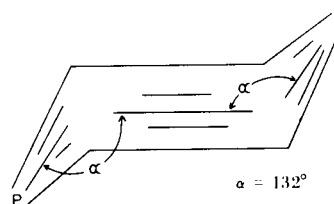


Figure 2

The C-C distances in the phenyl rings average  $1.39 \pm .02$  Å over the eight crystallographically unique phenyl rings with the rings individually averaging from 1.37-1.41 Å. The C-C-C angles in these phenyl rings average to 120

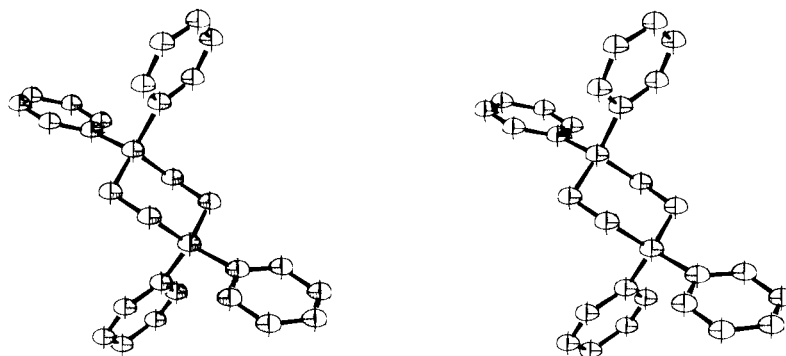


Figure 3 - ORTEP stereodrawing of the molecule.

$\pm 1^\circ$  overall or if averaged individually. Calculations of the best least-squares fit of each of the phenyl rings to a plane shows that these rings are essentially planar with ESD values ranging from 0.004-0.037 Å.

The value of the P-C distance ( $1.78 \pm .03$  Å) is in agreement with previous literature values (5) for this same parameter. The C-C distances of  $1.53 \pm .03$  Å within the central ring and the C-C distances of  $1.39 \pm .02$  Å in the phenyl rings conform respectively, with the accepted standard values of 1.54, 1.397 Å (6). An ORTEP stereodrawing of the molecule is given in Figure 3.

A bond scan of all intermolecular distances less than 4.0 Å in the unit cell shows no contacts less than 3.2 Å

between any two non-bromine atoms. The oxygen atom of the hydrated water molecule has two somewhat close distances to bromine atoms of adjacent molecules as shown in Figure 4. Although the angle approximates that in water indicative of hydrogen bonding, the distances are such as to suggest close-packing rather than any such interaction. There are no other light atom contacts with

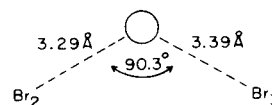


Figure 4

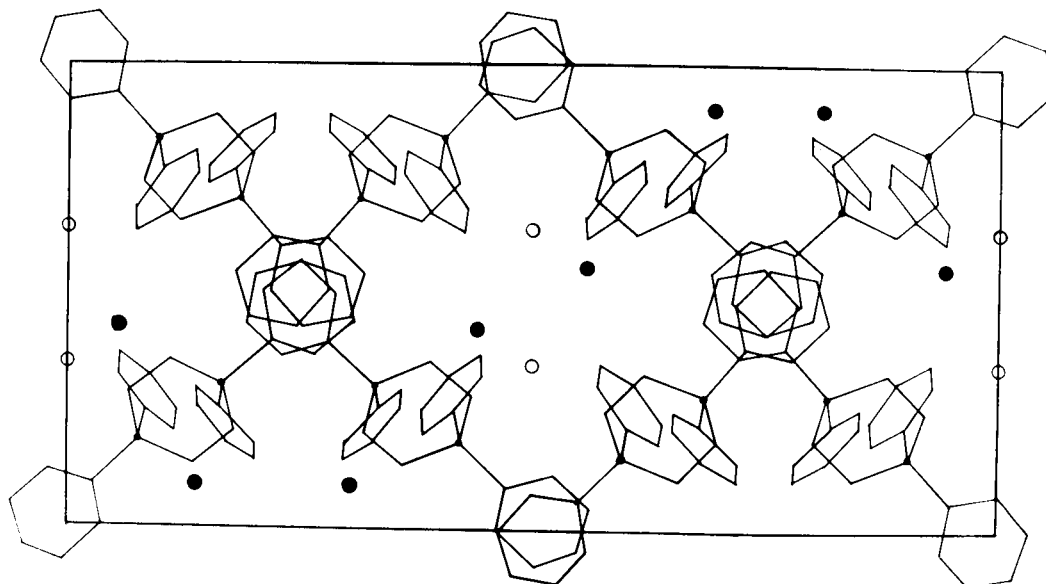


Figure 5 - Contents of the unit cell projected down the (001) axis. Long axis is the b-axis.

- oxygens of water molecules
- bromide ions

the bromines at distances less than 3.7 Å. All bromine-bromine and bromine-phosphorus distances are greater than 4.0 Å.

The original postulation of the preferential formation of this compound because of some inherent, unusual geometric feature thus is not correct. The conformation of the central ring system is in the chair form with bond distances and bond angles in conformity with previously accepted values. The two phenyl groups on each phosphorus atom assume the sterically least hindered orientation with each phosphorus atom having an axial and equatorial phenyl ring attached.

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