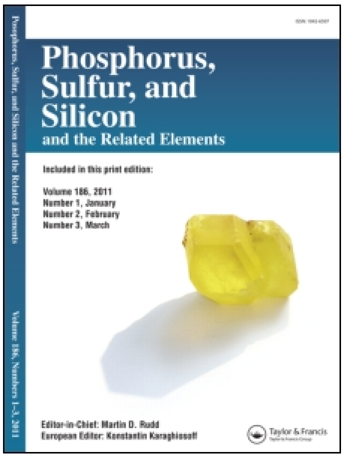

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STRUCTURAL CHARACTERIZATION OF 1,2,4,5-TETRAPHENYLCYCLO-3,6-DICARBA-1,2,4,5-TETRAPHOSPHINE: A HIGHLY FOLDED CHAIR CONFORMATION

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STRUCTURAL CHARACTERIZATION OF 1,2,4,5-TETRAPHENYLCYCLO-3,6-DICARBA-1,2,4,5-TETRAPHOSPHINE: A HIGHLY FOLDED CHAIR CONFORMATION

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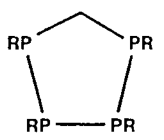
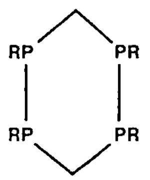
The title compound crystallized in the monoclinic space group $P2_1/c$, with the following unit cell parameters: $a = 11.235(8)$, $b = 8.473(2)$, $c = 26.136(10)$ Å, $\beta = 102.07(5)°$, $V = 2432(3)$ Å^3, $Z = 4$. 1657 unique data ($F_o^2 > 3\sigma(F_o^2)$) were used to solve (direct methods) and refine the structure to give $R = 0.126$ and $R_w = 0.118$. The six-membered ring system is in a highly folded chair conformation with the phenyl group substituents on the phosphorus atoms oriented in the equatorial positions. The dihedral angles of the P-CH$_2$-P plane with the P_4 basal plane is a remarkable 101.8° (average). This dihedral angle is the closest to perpendicular ever observed for a monocyclic ring system.

INTRODUCTION

There has been considerable interest in the chemistry of cyclocarba- and dicarbatetraphosphine species of the type $(RP)_4CH_2^1$ and $CH_2(PR)_4CH_2$.[2] Although a crystal structure on the 5-membered ring species $(PhP)_4CH_2$





has been reported[3] there have been no structural characterizations on the cyclohexane derivatives $CH_2(PR)_4CH_2$. Our work in the area of transition metal dimers based on the novel binucleating hexatertiary-phosphine ligand system $(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2$[4] has involved a considerable amount of exploratory organophosphorus chemistry and recent efforts to synthesize the analogous binucleating linear tetratertiary phosphine ligand $(R_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PR_2)$, LTTP,[5] lead to the isolation of a crystalline sample of cyclo-$CH_2(PhP)_4CH_2$, **1**, and the first structural characterization of a cyclo-3,6-dicarba-1,2,4,5-tetraphosphine species.

RESULTS AND DISCUSSION

The slow addition of KPHPh[6] to CH_2Cl_2 in THF produces bis(phenylphosphino)-methane $Ph(H)PCH_2P(H)Ph$, which is the key precursor in preparing LTTP, in ca. 25% yield. Interestingly this reaction has been previously reported by Issleib and coworkers *not* to yield any $Ph(H)PCH_2P(H)Ph$, but only polymethylene and the bisphosphine Ph(H)P-P(H)Ph.[6] An important consideration in Issleib's procedure, however, was that the CH_2Cl_2 was added *to* a suspension of KPHPh. We have previously observed in the synthesis of $Et_2P(CH{=}CH_2)$[4a] that the order of addition of the reactants can be critical and the same is true for this reaction as well.

Other products from the reaction of KPHPh and CH_2Cl_2 include the cyclophosphine species $(PhP)_4CH_2$ (20%) and $CH_2(PhP)_4CH_2$ (10%), along with the simple monophosphines PhPHMe (30%) and $PhPH_2$ (15%). Baudler and coworkers originally prepared **1** by the metallation of $(PhP)_4CH_2$ with potassium followed by reaction with one equivalent of CH_2Cl_2 (18% yield).[1g] Since $(PhP)_4CH_2$ is produced in this reaction, it is conceivable that $CH_2(PhP)_4CH_2$ is forming via a related mechanism. Cyclo-dicarbatetraphosphines have been most commonly isolated, however, as dimerization products of unstable diphosphacyclo-propane molecules.[2b,f–g] We have subsequently found that Stelzer's procedure for the preparation of $Ph(H)PCH_2P(H)Ph$ is superior in that higher yields (50–70%) and a cleaner reaction mixture are obtained, although the presence of the 5-membered ring species $(PhP)_4CH_2$ is observed under appropriate conditions.[7]

Two different types of crystals are obtained from the slow evaporation of a benzene solution of the cyclophosphines: cloudy and clear colorless crystals with different morphologies. An X-ray analysis on the cloudy crystals demonstrated the presence of the previously structurally characterized 1,2,3,4-tetraphenylcyclo-5-carba-1,2,3,4-tetraphosphine.[3] A structure on the clear crystals, however, proved to be that of the 6-membered ring 1,2,4,5-tetraphenylcyclo-3,6-dicarba-1,2,4,5-tetraphosphine, **1**. ^1H, ^{31}P and IR data for **1** agree with that reported by Baudler and coworkers.[1g] An ORTEP plot of **1** is shown in Figure 1 with selected bond distances and angles listed in Table I. There are two independent molecules in the asymmetric unit and each lies on a crystallographic inversion center.

The molecule adopts the expected chair conformation with the four phenyl rings occupying the equatorial sites and the smaller phosphorus lone pairs oriented in the more sterically demanding axial positions. A remarkable aspect of this structure is that the relatively small C-P-P angles of 96.1(4)° to 100.8(4)° significantly enhance the chair conformation as can be seen by the dihedral angles between the P_4 plane and the P1-C1-P2′ plane: 104.5° (molecule A) and 99.2° (molecule B). A side view of **1** with the phenyl groups omitted to highlight this highly folded chair conformation is shown in Figure 2.

These dihedral plane angles in **1** are the closest yet observed to 90° for a monocyclic system and can be contrasted to the considerably larger values of 129° for the chair form of cyclohexane,[8] 124.8° for 1,2,4,5-tetrabenzyl-3,6-dicarba-1,2,4,5-tetrazine,[9] and 134.4° for $(PhP)_4CH_2$.[3] The closest structurally characterized analog, however, is the sulfur derivative 3,3:6,6-bis(pentamethylene)-*s*-

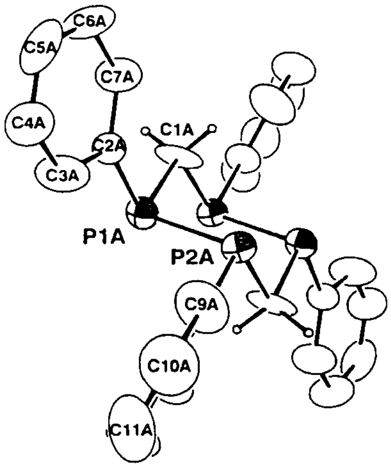


FIGURE 1 ORTEP plot of 1 (molecule A) in the crystal with thermal ellipsoids shown at the 33% probability level. The molecule lies on a crystallographic inversion center. Hydrogen atoms on the methylene bridge were calculated into idealized locations to show the geometry about these carbon atoms.

TABLE I

Selected bond distances (Å) and angles (deg) for 1 (molecules A and B)

	A	B
P1—P2	2.194(4)	2.230(4)
P1—C1	1.915(9)	1.89(1)
P1—C2	1.81(1)	1.91(1)
P2—C1	1.89(1)	1.91(1)
P2—C8	1.87(1)	1.85(1)
P2—P1—C1	100.8(4)	96.1(4)
P2—P1—C2	98.4(4)	96.8(3)
C1—P1—C2	101.2(5)	98.9(5)
P1—P2—C1	100.1(4)	95.3(4)
P1—P2—C8	98.9(4)	97.9(4)
C1—P2—C8	101.4(5)	102.7(5)
P1—C1—P2	104.9(5)	104.0(5)
P1—C2—C3	117(1)	108(1)
P1—C2—C7	129.1(9)	129(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

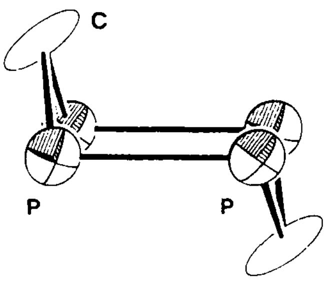


FIGURE 2 Structure of 1 (molecule A) with the phenyl groups and methylene group hydrogen atoms ommitted for clarity to show the highly folded nature of the 6-membered ring system.

tetrathiane which has a dihedral angle of 115.6°.[10] The methylene bridge P1-C1-P2′ angle in **1** is also somewhat contracted with an average value of 104.4(5)°. This can be compared to values of 116.9(1)° in $(PhP)_4CH_2$ and 108.0(1)° in 3,3:6,6-bis(pentamethylene)-*s*-tetrathiane.

EXPERIMENTAL

General. All manipulations were carried out under inert atmosphere (N_2 or Ar) using standard Schlenk or glove box techniques unless stated otherwise. Solvents were distilled under inert atmosphere from the following drying agents: diethyl ether, hexane, THF (sodium/benzophenone); toluene (sodium); CH_2Cl_2 and acetonitrile (CaH_2). ^{31}P and ^{1}H NMR spectra were run on a Bruker AC-100 spectrometer, IR spectra were run on a Perkin–Elmer 283B spectrometer.

Synthesis. A 30 mL THF solution/suspension of yellow-orange PhPHK[6] (10.07 g, 0.068 mol) is added dropwise very slowly (4–6 hours) via cannula to a magnetically stirred 40 mL THF solution of CH_2Cl_2 (2.89 g, 0.034 mol) at 0°C. The yellow-orange color discharges as the PhPHK is added to the CH_2Cl_2 solution. A white precipitate gradually formed as the addition proceeded. After the addition was complete the solution was allowed to stir for 2 hours and gradually warm to room temperature. The solution was concentrated by vacuum evaporation to ca. 20 mL. On standing the solid redissolved in the concentration solution. ^{31}P NMR spectrum of the solution clearly showed a mixture of five phosphorus containing species: $Ph(H)PCH_2P(H)Ph$ (25%), $PhPH_2$ (15%), PhP(H)Me (30%) and the cyclophosphine species $(PhP)_4CH_2$(20%) and $CH_2(PhP)_4CH_2$ (10%). Percent yields given are based on integrations from the ^{31}P NMR spectrum of the crude reaction mixture and are approximate. Cold (−40°C) diethyl ether was added to the solution causing a small amount of white precipitate to form. The solution was filtered to give a clear, slightly yellow solution.

Vacuum evaporation of this solution formed a white solid and a very viscous liquid. At this stage the liquid is primarily composed of $Ph(H)PCH_2P(H)Ph$, PhP(H)Me, and $PhPH_2$, while the solid is mainly a mixture of the two cyclophosphine species $(PhP)_4CH_2$ and $CH_2(PhP)_4CH_2$. Separation of the solid from the liquid by filtration, however, is rather difficult due to the very viscous nature of the

TABLE II

Crystallographic data for $CH_2(PhP)_4CH_2$, **1**.

Crystal Parameters

formula = $P_4C_{26}H_{24}$
crystal system = monoclinic
$a = 11.235$ (8) Å
$b = 8.473$ (2) Å
$c = 26.136$ (10) Å
$V = 2432$ (3) $Å^3$
$d_{calc} = 1.26$ g/mL
temperature = 21°C
cryst color = colorless

$fw = 460.38$
space group = $P2_1/c$
$\alpha = 90.00°$
$\beta = 102.07$ (5)°
$\gamma = 90.00°$
$Z = 4$
μ(Mo Kα) = 3.14 cm^{-1}
cryst size = 0.23 × 0.12 × 0.11 mm

Data collection and Structure Refinement

diffractometer = CAD4
monochromator = graph. cryst
scan method = $\theta/2\theta$
data limits = $3° < 2\theta < 40°$
reflcns collcd = 3611
weighting scheme = non-Poisson
params refined = 271
$R^a = 0.126$
$GOF^d = 3.03$
abs cor = yes

radiation = Mo(Kα)
attenuator = 17.5
scan speed = variable, 0.5–5°/min
octants collcd = h, k, $\pm l$
unique data, $F_0^2 > 3\sigma(F_0^2) = 1657$
fudge factor, P = 0.02
data/param ratio = 6.1
$R_w{}^b = 0.118$
max final shift/esd = 0.10
max final diff. Fourier pk., e/$Å^3$ = 0.78

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[a] $R = \sum ||F_0| - |F_c|| / \sum |F_0|$.
[b] $R_w = [\sum w(|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2}$; $w = 1/\sigma^2(|F_0|)$.
[c] Goodness of fit $= [\sum w(|F_0| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$

liquid. Mechanical separation by pipeting the liquid away from the solid works reasonably well. The solid can be washed with diethyl ether to give mainly the two cyclophosphine compounds (some Ph(H)PCH$_2$P(H)Ph is still present, however). Slow evaporation of a benzene solution of this solid gives two distinct crystal types: a cloudy colorless crystal that corresponds to the (PhP)$_4$CH$_2$ species and a clear, colorless crystal type that is CH$_2$(PhP)$_4$CH$_2$. A ^{31}P spectrum of the bulk crystals (after several were picked out for crystallographic analysis) showed that not only were the cyclophosphine species (PhP)$_4$CH$_2$ (61%) and CH$_2$(PhP)$_4$CH$_2$ (25%) present, but also *one* of the diastereomers of Ph(H)PCH$_2$P(H)Ph (14%). ^{31}P, ^{1}H and R spectroscopic data on these species agree with known literature values. ^{31}P NMR data (C$_6$D$_6$, ppm, H$_3$PO$_4$ ref): Ph(H)PCH$_2$P(H)Ph, −53.8 and −54.7 (two diastereomers); PhP(H)Me, −69.9; PhPH$_2$, −122.4; (PhP)$_4$CH$_2$, (AA'BB' second order pattern) 52.75, 52.54, 50.72, 50.36, 47.71, 47.53, 45.54, 40.48, 39.87, 29.73, 29.13, 23.96, 22.02, 21.80, 19.20, 18.82, 17.06, 16.85; CH$_2$(PhP)$_4$CH$_2$, −23.6.

X-ray Crystallography. Data was collected on an Enraf-Nonius CAD4 diffractometer at room temperature using Mo Kα radiation and a graphite crystal monochromator by $\theta/2\theta$ scan technique using variable speed scanning rates. Crystal data and experimental details are listed in Table II. Data reduction included corrections for background, Lorentz, and polarization effects, as well as an empirical absorption correction based on ψ scans of reflections near $\chi = 90°$. The structure was solved using direct methods and refined using the full-matrix least-squares technique. There are two molecules in the asymmetric unit and each lies on a crystallographic inversion center. Non-hydrogen positional parameters for **1** are listed in Table III. The small size of the crystal resulted in a small and not particularly good data set as indicated by the unusually high discrepancy indices and GOF parameter. In spite of this, the heavy atom framework of the molecule is well defined by the structure.

TABLE III

Positional parameters for CH$_2$(PhP)$_4$CH$_2$, **1**.

Atom	x	y	z	B(Å^2)
P1A	0.9248(5)	0.0806(6)	0.0513(2)	4.6(1)
P2A	0.8783(4)	−0.0724(6)	−0.0553(2)	4.4(1)
C1A	0.866(2)	0.123(2)	−0.0216(6)	6.2(6)
C2A	0.916(1)	0.275(2)	0.0791(6)	4.7(5)
C3A	0.936(2)	0.285(2)	0.1341(7)	7.5(6)
C4A	0.933(2)	0.426(2)	0.1589(7)	7.3(6)
C5A	0.907(2)	0.561(2)	0.1323(7)	8.0(6)
C6A	0.883(2)	0.561(2)	0.0775(8)	8.2(7)
C7A	0.890(2)	0.419(2)	0.0538(6)	6.8(6)
C8A	0.827(2)	−0.016(2)	−0.1258(6)	5.4(5)
C9A	0.767(2)	−0.118(3)	−0.1586(6)	7.9(7)
C10A	0.730(2)	−0.080(3)	−0.2098(8)	9.5(8)
C11A	0.762(2)	0.058(3)	−0.2283(6)	9.6(8)
C12A	0.822(2)	0.172(3)	−0.1972(7)	9.9(8)
C13A	0.864(2)	0.136(3)	−0.1420(7)	8.8(7)
P1B	0.4850(4)	−0.0237(6)	0.0690(2)	4.2(1)
P2B	0.4398(5)	−0.1857(6)	−0.0349(2)	4.5(1)
C1B	0.552(2)	−0.176(2)	0.0308(6)	5.8(5)
C2B	0.605(1)	−0.031(2)	0.1330(6)	3.9(4)
C3B	0.542(2)	−0.014(3)	0.1767(8)	11.7(9)
C4B	0.644(2)	−0.020(3)	0.2276(7)	11.9(9)
C5B	0.750(2)	−0.043(3)	0.2304(8)	9.5(7)
C6B	0.795(2)	−0.061(3)	0.1882(7)	6.8(6)
C7B	0.719(1)	−0.056(2)	0.1400(6)	5.4(5)
C8B	0.506(1)	−0.341(2)	−0.0703(5)	4.6(4)
C9B	0.626(2)	−0.383(2)	−0.0598(6)	5.5(5)
C10B	0.673(2)	−0.503(2)	−0.0878(7)	7.9(6)
C11B	0.591(2)	−0.573(2)	−0.1259(6)	5.9(5)
C12B	0.472(2)	−0.534(2)	−0.1379(6)	6.6(6)
C13B	0.424(2)	−0.419(2)	−0.1097(6)	5.7(5)

Atoms labeled A and B belong to the two independent molecules in the asymmetric unit. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)[a^{2}B(1, 1) + b^{2}B(2,2) + c^{2}B(3,3) + ab(cos γ)B(1,2) + ac(cos β) B(1, 3) + bc(cos α)B(2, 3)]

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