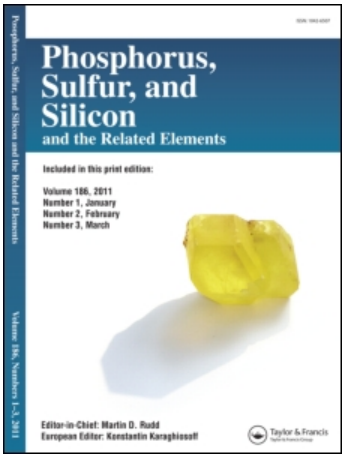

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STRUCTURAL STUDIES OF *N-N*-BIS(DICHLOROPHOSPHINO) PHENYLAMINES

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STRUCTURAL STUDIES OF *N*-*N*-BIS(DICHLOROPHOSPHINO)PHENYLAMINES

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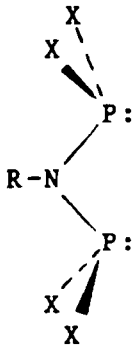
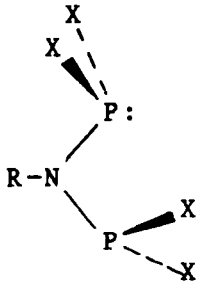
The structural characterization of $PhN(PCl_2)_2$ and $m\text{-}MeC_6H_4N(PCl_2)_2$ in solution by ^{31}P NMR spectroscopy and of $PhN(PCl_2)_2$ in the solid by single crystal X-ray analysis is reported. $PhN(PCl_2)_2$ adopts a C_{2v} conformation in the solid, in which the phosphorus lone pair electrons are eclipsed and both trans to the Ph group. The C_{2v} conformation assignment for $PhN(PCl_2)_2$ and $m\text{-}MeC_6H_4N(PCl_2)_2$ is consistent with the low temperature ^{31}P NMR spectral data. $PhN(PCl_2)_2$ crystallizes in space group $P2_1$, a = 6.360(2) Å, b = 25.618(11) Å, c = 7.146(2) Å, β = 90.62(2) deg, Z = 4, with two independent molecules per unit cell. The structure was solved and refined by direct methods to R = 0.058 and R_w = 0.078 for 671 independent reflections. Mean distances (Å) and angles (deg) are: P—Cl, 2.036(13); P—N, 1.69(3); ∠P—N—P, 110.8(8); and ∠Cl—P—Cl, 100.1(6).

INTRODUCTION

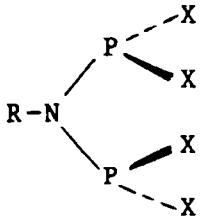
Diphosphinoamine (**1**) coordination,[2] formation,[3-6] and structural[4,6-9] chemistry has received considerable attention recently. Structural studies have been particularly interesting because, from them detailed information about molecular conformation has been obtained. It is now generally recognized that three limiting conformations of diphosphines are most likely (**1a–1c**), conformations in which phosphorus and nitrogen atom lone pair electrons are orthogonal.[3,9] Based on electron diffraction, NMR spectral, and to a lesser extent X-ray diffraction studies, it has been



1a; C_{2v}



1b; C_s



1c; C_{2v}'

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established that with relatively small R and X groups conformer **1a** is most stable. With larger R groups conformer **1b** predominates. Well characterized examples of **1c**, presumed to involve high intramolecular group repulsions, are so far unknown.

Keat and coworkers[4] examined the bis(dichlorophosphino)amine series $RN(PCl_2)_2$ (R = Me, Et, *t*-$BuCH_2$ and *t*-Bu) and showed, based on $^2J_{PNP}$ coupling constant data, that when R = Me and Et, the C_{2v} conformer is favored. When R = *t*-$BuCH_2$ or *t*-Bu, the C_s form predominates. Unfortunately, no examples of aryl substituted species (R = aryl) were examined.

Since *N*-aryl $RN(PCl_2)_2$ compounds are important in the synthesis of novel *N*-aryl substituted 1,3,2,4-diazadiphosphetidines[10,11], in the newly-demonstrated diastereoselective synthesis of diphosphinomamines,[12] and possibly in the formation of new phosphazane macromolecules, their conformational properties have become of particular interest. Because the phenyl group (i) is approximately intermediate in size between the Et and *t*-$BuCH_2$ groups and (ii) could show unique electronic interactions with the central N atom of **1**, we undertook a study of the conformational properties of two diphosphinoamines, $PhN(PCl_2)_2$ (**2**) and *m*-$MeC_6H_4N(PCl_2)_2$ (**3**) in solution and $PhN(PCl_2)_2$ in the solid state. Our results are described below.

RESULTS AND DISCUSSION

The structure of $PhN(PCl_2)_2$ (**2**) in the solid, as determined by single crystal X-ray analysis, is shown in Figure 1. **2** crystallizes in the monoclinic space group $P2_1$ with two independent, almost identical molecules per asymmetric unit. The packing of $PhN(PCl_2)_2$ molecules in the unit cell is shown in Figure 2. No significant intermolecular interactions, which could cause clear preference for a particular conformation in the solid, are apparent.

Compound **2** contains two PCl_2 groups bonded to the PhN unit such that the lone pair electrons on phosphorus are essentially eclipsed. **2** is in conformation **1a** and has approximate point group symmetry C_{2v}. The dihedral angles between perpendiculars to the Cl(1), Cl(2), N(1) and Cl(3), Cl(4), N(1) planes are 8.1(5) for molecule 1 and 6.5(5) for molecule 2. Bond angles around phosphorus atoms are typical,[3,20] between pyramidal and tetrahedral as expected for a $-\ddot{P}Cl_2$ unit. The N atom, within experimental error, is trigonal planar and in the C(1), P(1), P(2) plane. The phenyl ring is almost perpendicular to the C(1), P(1), P(2), N(1) plane; dihedral angles 87.8(5)°, molecule 1, and 88.5(5)° molecule 2. The P—Cl bond distances (Table I) are similar to those in other P(III)—Cl bond containing molecules [*eg.* 2.09 Å in *cis*-$(C_6H_5NPCL)_2$].[21] The mean skeletal P—N bond distances of 1.69(3) Å in **2** are within experimental error, 1.670(5) Å, of those in the phenylamino substituted analog $C_6H_5N[P(NHC_6H_5)_2]_2$.[22] The mean ∠P—N—P in **2** (110.8°) is smaller than in $PhN[P(NHPh)_2]_2$ (117.7°),[22] an effect which may in part be related to substituent electronegativity differences in the two cases.

The ^{31}P NMR spectra of $PhN(PCl_2)_2$ (**2**) and *m*-$C_6H_4N(PCh)_2$ (**3**) in toluene in the temperature range 25°C to −90°C were obtained. Over the entire range both exhibit only sharp singlet resonances. The resonance for **2** shifts from δ 155.6 ppm at 25°C to δ 151.4 ppm at −90°C, with no indication of splitting into two resonances. The resonance half height width ($\nu_{1/2}$) decreases from 8 Hz at 25°C to 5 Hz at

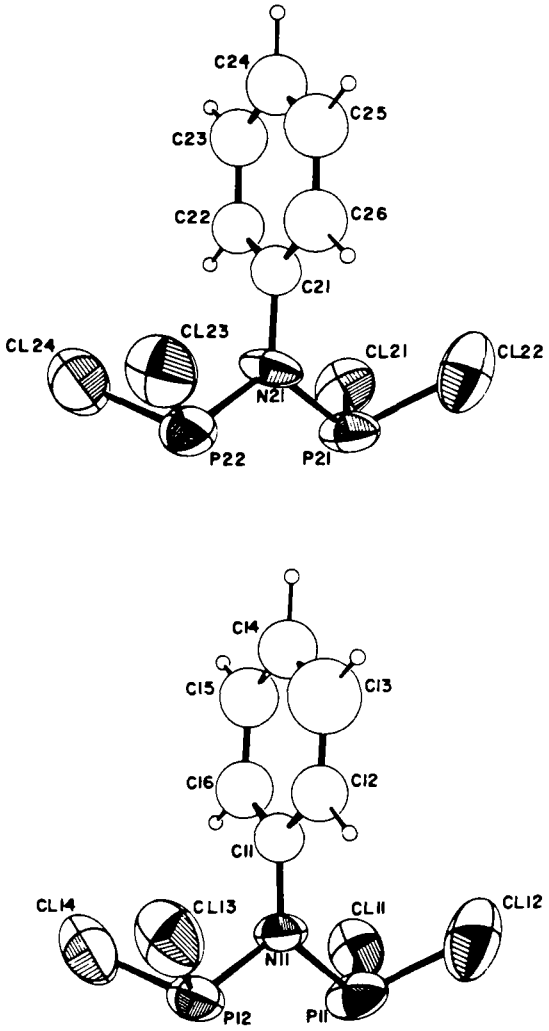

FIGURE 1 The solid state structure of $PhN(PCl_2)_2$ (**2**) showing the numbering scheme adopted. The two independent molecules, 2 and 1, are shown at the top and bottom, respectively of the figure. Thermal elipsoids are shown at the 50% probability level for both isotropic and anisotropic atoms. The hydrogen atoms are shown with an arbitrary radius for clarity.

−90°C. **3** behaves similarly, the ^{31}P NMR resonance shifts from δ 155.5 ppm at 25°C to δ 151.6 ppm at −90°C.

The limiting conformations of **2** and **3** which can be expected, based on earlier studies of diphosphinoamines, are **1a** and **1b**, above. Since P—N bond rotation barriers are generally *ca* 10–15 kcal/mol,[9,20,23] "freezing" of **2** and **3** to a restricted conformation at −90°C is assumed. Since the ^{31}P NMR spectra remain symmetrical, and in fact sharpen at lower temperatures, the presence of significant quantities of the unsymmetrical C_s conformation **1b** at any temperature seems unlikely. Such a conformation would be expected to show two phosphorus atom resonances and have a $^2J_{PNP}$ of *ca* 20 Hz[4] which would cause significant line broadening even in low

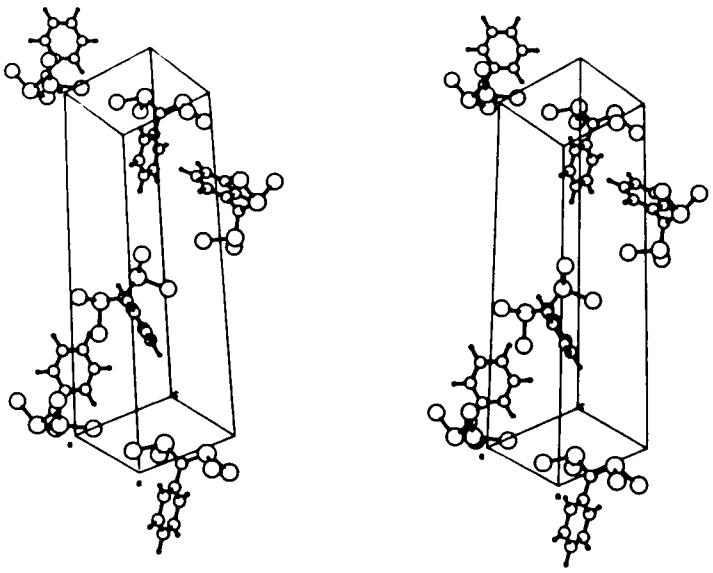

FIGURE 2 A stereo view of packing in the unit cell of $PhN(PCl_2)_2$ (**2**).

TABLE I

Bond Lengths (Å) and Bond Angles (deg) in **2**

(a) *Bond Lengths*			
P(11)—Cl(11)	2.048(8)	P(21)—Cl(21)	2.036(8)
P(11)—Cl(12)	2.031(9)	P(21)—Cl(22)	2.036(9)
P(12)—Cl(13)	2.040(9)	P(22)—Cl(23)	2.009(9)
P(12)—Cl(14)	2.035(9)	P(22)—Cl(24)	2.056(9)
P(11)—N(11)	1.687(15)	P(21)—Nl(21)	1.701(14)
P(12)—N(11)	1.719(16)	P(22)—N(21)	1.641(15)
N(11)—C(11)	1.437(18)	N(21)—C(21)	1.441(17)
(b) *Bond Angles*			
Cl(11)—P(11)—Cl(12)	97.5(4)	Cl(21)—P(21)—Cl(22)	97.3(3)
Cl(11)—P(11)—N(11)	103.6(6)	Cl(21)—P(21)—N(21)	103.8(6)
Cl(12)—P(11)—N(11)	100.9(6)	Cl(22)—P(21)—N(21)	102.6(6)
Cl(13)—P(12)—Cl(14)	98.3(4)	Cl(23)—P(22)—Cl(24)	97.5(4)
Cl(13)—P(12)—N(11)	100.8(6)	Cl(23)—P(22)—N(21)	103.0(6)
Cl(14)—P(12)—N(11)	102.3(6)	Cl(24)—P(22)—N(21)	103.3(6)
P(11)—N(11)—P(12)	109.4(8)	P(21)—N(21)—P(22)	112.1(8)
P(11)—N(11)—C(11)	127(1)	P(21)—N(21)—C(21)	122(1)
P(12)—N(11)—C(11)	123(1)	P(22)—N(21)—C(21)	126(1)

concentrations. Because **2** prefers the C_{2v} conformation (**1a**) in the solid, and does not appear forced into it by packing or other intermolecular forces, we conclude that **1a** is the lowest energy structure for **2**. Conformation **1a** is the dominant conformation assumed by both **2** and **3** in solution when "frozen" at low temperatures and over the temperature range 25°C to −90°C. Thus, **2** and **3** show a conformational preference similar to $MeN(PCl_2)_2$ and $EtN(PCl_2)_2$, but different from *t*-$BuCH_2N(PCl_2)_2$ and *t*-$BuN(PCl_2)_2$.[4]

Compound **3** could become unsymmetrical in conformation **1a**, if restricted rotation around the *m*-MeC_6H_4—N bond occurred in such a way as to remove the symmetry plane between PCl_2 groups. Since no asymmetry in the ^{31}P NMR resonance of **3** is seen at −90°C, we conclude that either the molecule freezes into a C_{2v} conformation or free rotation around the C—N bond is maintained. The latter seems preferable, since the barrier to rotation around the *m*-MeC_6H_4C—N bond might be expected to be low (< 5 kcal/mole).[24]

Many $RN(PCl_2)_2$ reactions occur at or below 25°C; therefore, it is reasonable to conclude that conformation **1a** is a major reacting species in these reactions. To the extent this conformational tendency is general for bis(chlorophosphino)amine species, it could be a factor in understanding mechanistic details of diazadiphosphetidine specific isomer formation reactions[9,21,22] and diastereoselective formation of unsymmetrically substituted [*ie.* $RN(PXY)_2$] bis(phosphino)amines.[12] Further examination of these concepts is in progress currently in our laboratories.

TABLE II

Experimental Details of the X-Ray Diffraction Study of $C_6H_5N(PCl_2)_2$ (**2**)

(a) *Crystal Data*	
fw: 294.873	V, Å^3: 1164.3(7)
space group: $P2_1$	D_{calc}, g cm^{-3}; 1.682
a, Å: 6.360(2)[a]	D_{obs}[b], g cm^{-3}; 1.64
b, Å: 25.618(11)	Z: 4
c, Å: 7.146(2)	temp: 24°C
β, deg: 90.62(2)	F(000): 584
(b) *Measurement of Intensity Data*	
radiation, Å	MoK_α, λ = 0.71069
scan mode	θ–2θ
2θ angular range, deg	$3 \leq 2\theta \leq 35$
scan speed, deg min^{-1}	4.0 to 24.0
background mode	stationary crystal-stationary counter
background time/scan time	0.5
reflections measured	766
(c) *Structure Refinement*	
reflections obsd[c]	671
number variables	150
observations/variables	4 : 1
R	0.058
R_ω	0.078

[a] Estimated standard deviations shown in parentheses in this and subsequent tables are of the least significant digits of the proceeding number.
[b] Measured using the floatation (CCl_4 + C_2H_5I) method.
[c] $F_0^2 \geq 3.0\sigma(F_0^2)$

EXPERIMENTAL SECTION

Apparatus and Materials. All operations were carried out in N_2-flushed glove bags or in evacuated systems.[13] ^1H NMR were obtained at 90.0 and 250.0 MHz using JEOL-FX90Q and Bruker WM-250 spectrometers, respectively. ^{31}P NMR were obtained at 36.1 and 89.6 MHz using JEOL-FX90Q and Bruker WM-250 spectrometers. Variable temperature spectra were measured on the Bruker spectrometer. ^1H and ^{31}P NMR chemical shifts were measured relative to internal Me_4Si and external H_3PO_4, respectively. Chemical shifts downfield from the standard are given positive ($+\delta$) values. Infrared and mass spectra were obtained using Beckman and Varian MAT CH5 spectrometers, respectively. Single crystal X-ray data were collected at ambient temperature using a Syntex $P\bar{1}$ automated diffractometer equipped with a graphite monochromator.

Bis(dichlorophosphino)phenylamine (**2**) was prepared as described previously.[14] The *m*-$MeC_6H_4N(PCl_2)_2$ (**3**) was prepared analogously (see characterization below). Phosphorus trichloride and *m*-$MeC_6H_4NH_2$ were distilled before use. Benzene and toluene were distilled from Na/Pb alloy and stored under N_2. Chloroform and CH_2Cl_2 were distilled from P_4O_{10}.

Characterization of m-$MeC_6H_4N(PCl_2)_2$ (**3**). Recrystalization from petroleum ether yields pure **3** (mp 42–45°C); ^{31}P NMR (C_7D_8), δ 155.5 ppm(s); ^1H NMR (C_6D_6), δ 7.04–6.92 ppm (complex), δ 2.03 (s). Mass spectrum (rel. int.), parent and five intense ion envelopes, m/e 309(25), 272 (10), 171(50), 136(100) and 91(30).

X-Ray Analysis of $C_6H_5N(PCl_2)_2$ (**2**). Clear needles of **2** were obtained by recrystallization from toluene (mp 45–46°C; lit.[14] 45–46°C). Data were collected on a parallelpiped crystal (0.30 mm × 0.30

TABLE III

Positional and Thermal Parameters for $C_6H_5N(PCl_2)_2$

Atom[a]	X/A	Y/B	Z/C	U_{eq} or U[b]
Cl(11)	.175(1)	.0298(2)	.0762(8)	.090(3)
Cl(12)	−.285(1)	.0631(3)	.023(1)	.121(3)
Cl(13)	−.053(1)	.1502(3)	−.5862(8)	.103(3)
Cl(14)	.390(1)	.1095(3)	−.4852(9)	.108(3)
Cl(21)	.6615(9)	−.0270(2)	.4278(8)	.083(3)
Cl(22)	.2088(9)	−.0657(3)	.459(1)	.105(3)
Cl(23)	.450(1)	−.1499(2)	1.0790(8)	.097(3)
Cl(24)	.886(1)	−.1073(3)	.9899(9)	.104(3)
P(11)	−.040(1)	.0394(2)	−.1364(8)	.079(3)
P(12)	.085(1)	.0861(2)	−.4680(8)	.078(3)
P(21)	.444(1)	−.0394(2)	.6299(7)	.072(3)
P(22)	.576(1)	−.0862(2)	.9608(8)	.076(3)
N(11)	.032(3)	.0963(5)	−.236(2)	.071(7)
N(21)	.528(2)	−.0951(5)	.737(2)	.059(6)
C(11)	.068(2)	.1452(4)	−.142(2)	.058(5)
C(12)	−.104(2)	.1791(4)	−.140(2)	.070(6)
C(13)	−.088(2)	.2269(4)	−.047(2)	.115(9)
C(14)	0.98(2)	.2407(4)	.044(2)	.079(7)
C(15)	.270(2)	.2068(4)	.042(2)	.076(6)
C(16)	.255(2)	.1591(4)	−.051(2)	.075(6)
C(21)	.557(2)	−.1431(4)	.635(2)	.054(5)
C(22)	.751(2)	−.1528(4)	.554(2)	.064(6)
C(23)	.787(2)	−.1999(4)	.462(2)	.078(6)
C(24)	.628(2)	−.2372(4)	.450(2)	.083(7)
C(25)	.433(2)	−.2275(4)	.531(2)	.088(7)
C(26)	.397(2)	−.1804(4)	.623(2)	.081(7)

[a] Carbon atom positional parameters given are derived from rigid group parameters.

[b] The equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Thermal parameters for carbon atoms are isotropic U's.

mm × 0.5 mm) mounted in and coated with epoxy resin. Crystal data, intensity data, and refinement results are summarized in Table II. Cell parameters were determined on the diffractometer and refined by least squares fit to fifteen centered reflections.

The data set was collected to only $2\theta = 35°$ because of marginal crystal quality and stability. The data were corrected for Lorentz and polarization effects,[15] but not for absorption ($\mu MoK_\alpha = 12.49\ cm^{-1}$). Anisotropic positional and thermal parameters are shown in Table III. The structures were solved by direct methods[16] and refined using full-matrix least-squares techniques[17] with the phenyl rings treated as rigid groups with individual isotropic thermal parameters. There are two independent molecules in the asymmetric unit in space group $P2_1$. These two molecules are related by a pseudo-symmetry operation $1/2 + x, -y, 1/2 - z$ which leads very nearly to the space group $P2_12_12_1$.[18] Careful comparison of the reflections hkl and $hk\bar{l}$, which should be equivalent in the orthorhombic case, showed that, of 280 reflections measured more than once, 168 had discrepancies greater than three times their standard deviations. This, combined with the β angle of 90.62°, supports the choice of the monoclinic cell. In addition, we have refined the model in space group $P2_12_12_1$. The calculation, which converged to a higher final residual ($R = 0.081$; $\omega R = 0.119$), resulted in a model which showed the same geometrical features.[19]

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$$SUM\left\{ w(F_0| - |F_c|)^2 \right\}.$$

$$R_1 = SUM||F_0| - |F_c||/SUM|F_0|$$

$$R_2 = \left[SUM\left\{ w(|F_0| - |F_c|)^2 \right\} / SUM\left\{ w(F_0)^2 \right\} \right]^{1/2}$$

18. One of the authors (RCH) wishes to thank Dr. R. E. Marsh, Department of Chemistry, California Institute of Technology, for a helpful discussion of this pseudo symmetry.
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