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# Unsymmetrical and Symmetrical Diphosphazane Ligands Derived from *o*-Phenylene Phosphorochloridite

Ruppa P. Kamalesh Babu, Setharampattu S. Krishnamurthy,* and Munirathinam Nethaji

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India*

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## ABSTRACT

*Two new diphosphazane ligands,* $\mathrm{Pr^iN(PPh_2)(PO_2C_6H_4)}$ (**1**) *and* $\mathrm{Pr^iN\{P(O_2C_6H_4)\}_2}$ (**3**), *have been synthesized and characterized by spectroscopic data. The structure of* **1** *has been confirmed by single crystal X-ray diffraction. Crystal data: Monoclinic,* C2/c, Z = 16, $a = 34.149(5)$ Å, $b = 9.717(6)$ Å, $c = 29.439(5)$ Å, $\beta = 125.11(2)°$, $V = 7991$ Å$^3$, $R = 0.058$, $R_w = 0.061$. *This compound shows two different P–N bond lengths (1.654 (4) and 1.743(4) Å) and a P–N–P angle of 120.7(2)°. Variable temperature* $^{31}$P *NMR measurements for* **1** *and* **3** *throw light on the nature of the conformers present in solution.*

## *INTRODUCTION*

Diphosphazanes containing the P–N–P framework offer considerable scope as ligands for designing homo or hetero bimetallic complexes that may function as homogeneous catalysts [1–4]. Whereas considerable work has been carried out on symmetrically substituted diphosphazanes of the type $\mathrm{X_2PN(R)PX_2}$, studies on diphosphazanes containing differently substituted phosphorus centers are sparse [5, 6]. These unsymmetrically substituted diphosphazanes are advantageous in that the phosphorus–phosphorus coupling constant in the free ligand as well as in their transition metal complexes can be obtained directly from their $^{31}$P NMR spectra. In this paper, we report the synthesis and spectroscopic characterization of the new diphoshazanes, $\mathrm{Pr^iN(PPh_2)(PO_2C_6H_4)}$ (**1**) and $\mathrm{Pr^iN\{P(O_2C_6H_4)\}_2}$ (**3**), derived from *o*-phenylene phosphorochloridite. The structure of the unsymmetrical diphosphazane **1** has been confirmed by single crystal X-ray diffraction.

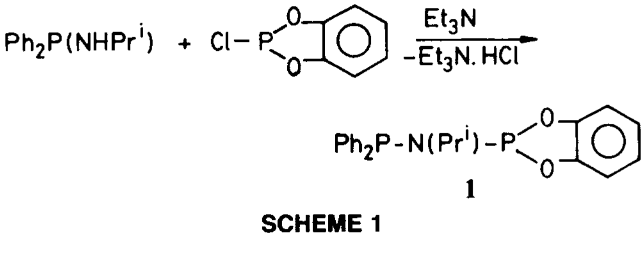
## *RESULTS AND DISCUSSION*

### *Preparative Aspects*

The unsymmetrical diphosphazane ligand, $\mathrm{Pr^iN(PPh_2)(PO_2C_6H_4)}$ (**1**), is prepared by the reaction of (isopropylamino)diphenylphosphine with *o*-phenylene phosphorochloridite in the presence of triethylamine as hydrogen chloride acceptor (Scheme 1). The method is analogous to that reported by Keat and co-workers for the preparation of $\mathrm{Pr^iN(PPh_2)_2}$ [5].

The symmetrical diphosphazane ligand bis(*o*-phenylenedioxyphosphino)isopropylamine (**3**) has been obtained by a two-step synthesis as shown in Scheme 2.

Compound **1** is a colorless crystalline solid mod-



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**SCHEME 1**

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Dedicated to Prof. Marianne Baudler on the occasion of her seventieth birthday.

*To whom correspondence should be addressed.

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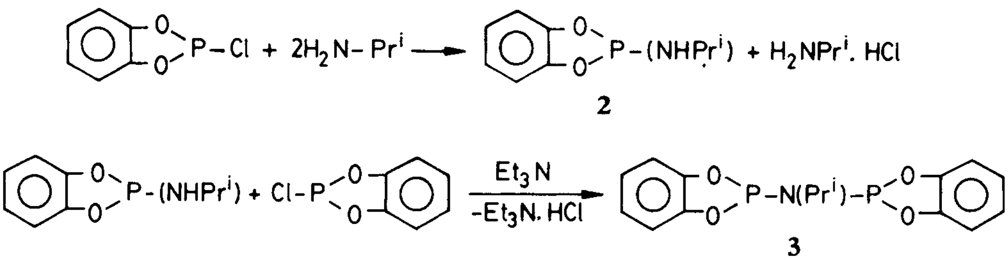


**SCHEME 2**

erately stable in air. Both **2** and **3** are highly air-sensitive; compound **2** exudes an unpleasant smell. Diphosphazane ligands akin to **3** but with aliphatic dioxy groups have recently been reported [3, 4].

### *Spectroscopic Data*

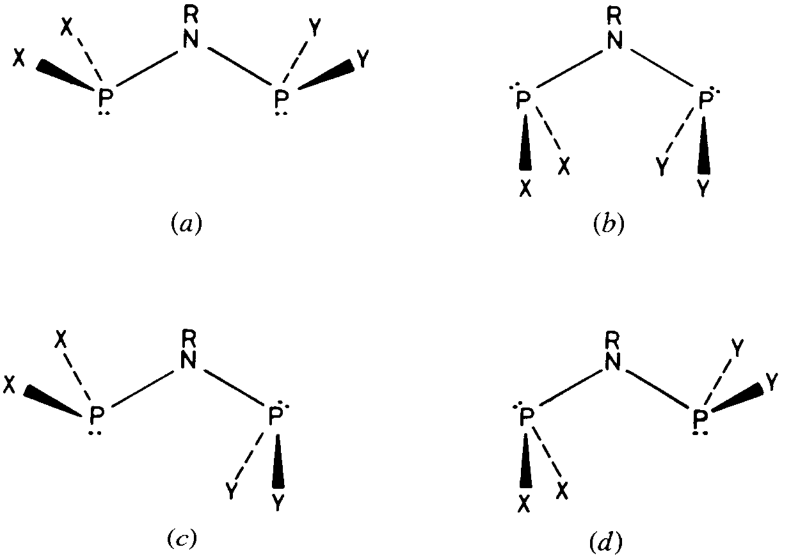
The $^{31}P\{^{1}H\}$ NMR spectrum of **1** at ambient temperatures is of a simple AX type, with a $^{2}J(PNP)$ coupling of 14 Hz. The chemical shifts of $PPh_2$ and $P(O_2C_6H_4)$ are $\delta$ 28.9 and 155.8, respectively. The $^{31}P\{^{1}H\}$ NMR spectrum of compounds **2** or **3** consists of a singlet and the chemical shifts (139.5, 149.9, respectively) are in the expected region for a $\lambda^3$-phosphorus bonded to two oxygen atoms and one nitrogen atom.

The resonances observed in the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectrum of **1** can readily be assigned by a comparison of the observed chemical shifts with those observed for the symmetrical diphosphazane **3**. The *ipso*-carbon atoms of the $C_6H_5$ groups appear as a doublet of doublets with $J_{PC}$ values of 14.2 and 10.2 Hz; the *ipso*-carbon atoms of the $O_2C_6H_4$ unit show only a doublet with a $^{2}J_{PC}$ value of 7.2 Hz.

Previous studies [5–7] have shown that there are three idealized conformations ($C_{2v}$, $C_s$, and $C'_{2v}$) for diphosphazanes of the type $X_2PN(R)PX_2$. For an unsymmetrically substituted diphosphazane of the type $X_2PN(R)PY_2$, we have to consider four idealized conformations *a–d* as shown in Scheme 3. For a symmetrically substituted diphosphazane of the type $X_2PN(R)PX_2$, conformers *c* and *d* would be identical.

Compound **1** adopts conformation *c* ($X_2 = O_2C_6H_4$, $Y = Ph$) in the solid state in which the lone pair on $PPh_2$ is cis to the N–C bond (see below for crystal structure results). Variable temperature $^{31}P$ NMR measurements have been carried out for $Pr^iN\{P(O_2C_6H_4)\}_2$ (**3**) and $Pr^iN(PPh_2)(PO_2C_6H_4)$ (**1**) to ascertain the nature of the conformational equilibrium in solution. The spectra are illustrated in Figures 1 and 2.

For the symmetrical compound **3**, a singlet is observed at room temperature that persists even at 195 K. We assign this signal to conformer *a* ($X_2 = Y_2 = O_2C_6H_4$). In addition, at 195 K, another singlet and two broad signals are observed that may be attributed to conformers *b* and *c*, respectively (Fig-



(*a*) (*b*)

(*c*) (*d*)

**SCHEME 3**

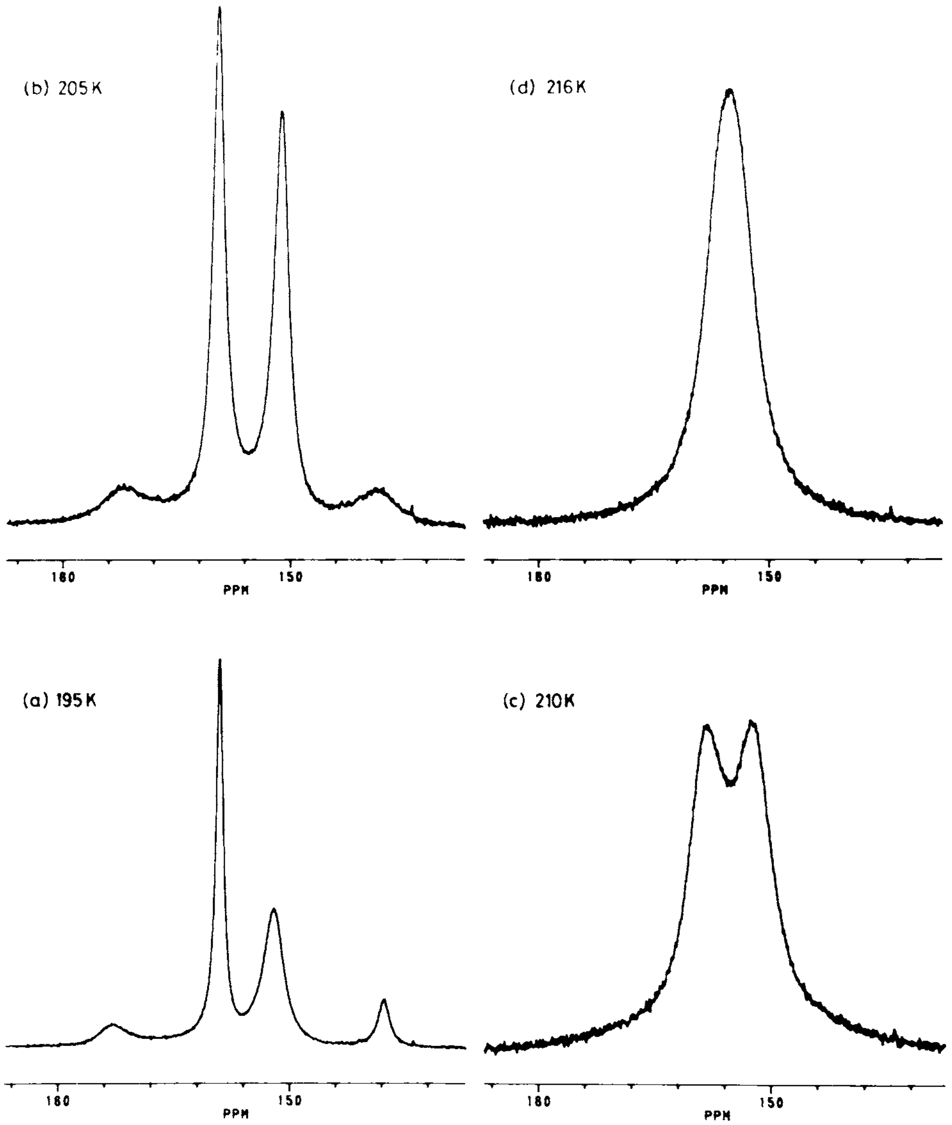


**FIGURE 1** The $^{31}P\{^1H\}$ NMR spectra (solvent tetrahydrofuran; 80.1 MHz) of $Pr^iN\{P(O_2C_6H_4)\}_2$ (**3**) at various temperatures.

ure 1). The lines broaden as the temperature increases and coalescence occurs at 213 ± 2 K. A further increase in temperature sharpens the signal.

For the unsymmetrical compound **1** the spectrum at 195 K shows a broad singlet for the $P(O_2C_6H_4)$ group at $\delta$ 157.2, whereas for the $PPh_2$ center a doublet is obtained at $\delta$ 25.8 (Figure 2). At 205 K, sharp doublets are seen for both phosphorus centers. The low coupling ($^2J_{PP}$ = 29.2 Hz) indicates that the conformer *c* found in the solid state predominates in solution [6, 7]. In addition to these pairs of doublets, another pair of resonances (not shown in Figure 2) are observed at $\delta$ 162.5 (doublet, $^2J_{PP} \sim 100$ Hz) and 42.9 (broad); the total intensity of this set of signals is less than 2% of that of the major signals mentioned above. The minor set of peaks disappears on increasing the temperature to 235 K; at 245 K, there is a broadening of the doublet at $\delta$ 25.8 arising from the $PPh_2$ group to a broad singlet. However, at 275 K, the $P(O_2C_6H_4)$ and $PPh_2$ signals appear as doublets with a $^2J_{PP}$ value of 17.5 Hz, which decreases to 13.5 Hz upon increase of the temperature to 315 K. At 345 K both signals appear as broad singlets.

An earlier study by Keat and co-workers reveals that the symmetrical compound $Ph_2PN(Pr^i)PPh_2$ exists as conformer *c* at low temperatures (210 K) (two doublets at $\delta$ 52.9 and 39.6 with a $^2J_{PP}$ of 23.9 Hz) [7]. These signals begin to broaden with an increase in temperature, and a single broad line is observed at temperatures above 283 K.

The above results are consistent with the interpretation that the barrier to rotation around the P–N bond at the $P(O_2C_6H_4)$ center is much less than

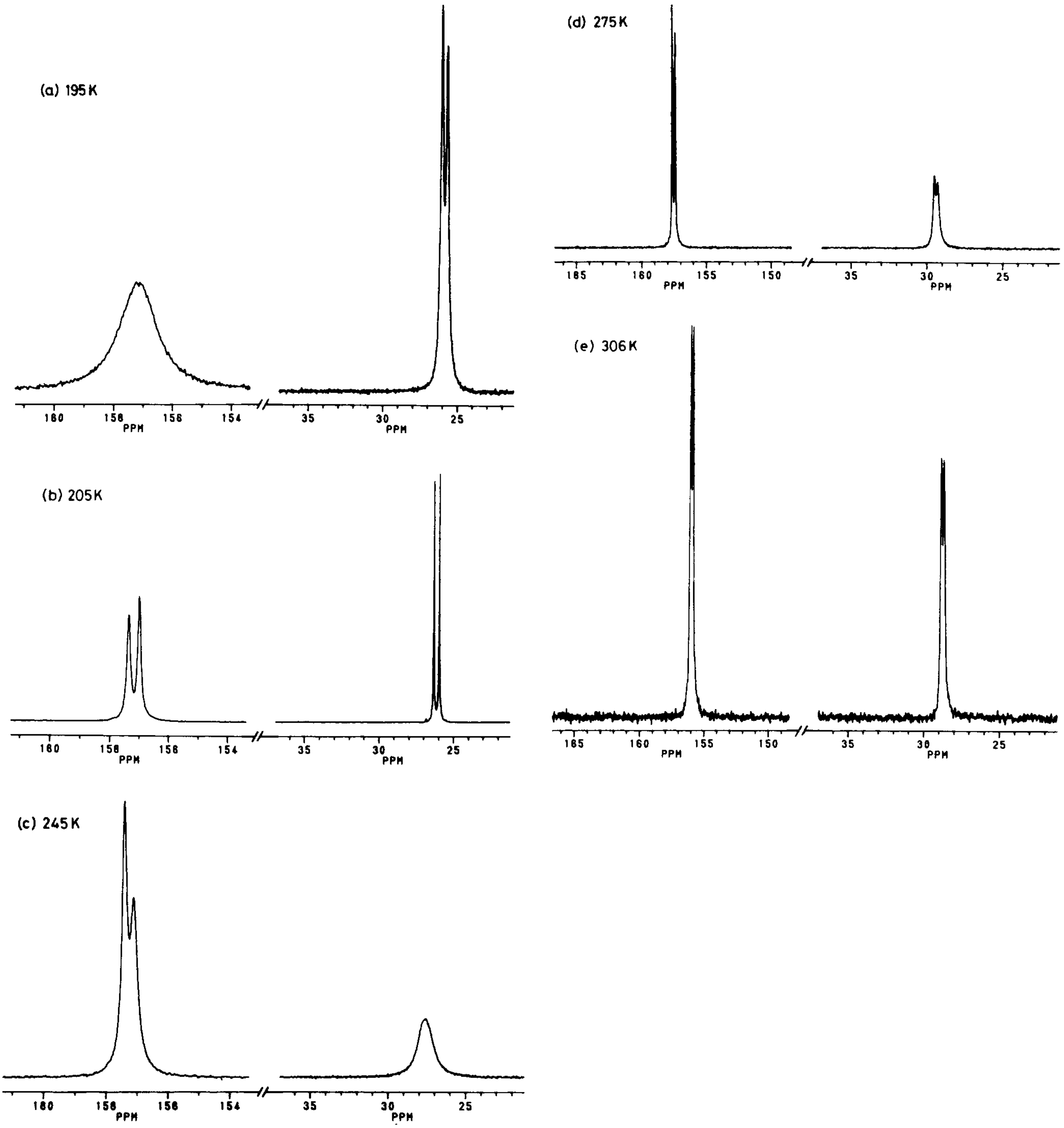


**FIGURE 2** The $^{31}P\{^1H\}$ NMR spectra (solvent toluene; 80.1 MHz) of $Pr^iN(PPh_2)(PO_2C_6H_4)$ (**1**) at various temperatures.

the barrier at the $PPh_2$ center. (Approximate $T_c$ for the symmetrical compounds $((C_6H_4O_2)P]_2NPr^i$ (**3**) and $(PPh_2)_2NPr^i$ are 212 K and 280 K, respectively.) For the unsymmetrical compound (**1**), which contains both these centers, the two rotational processes can be considered independent of each other, and, as a result, differential broadening effects are observed for the signals arising from the $PPh_2$ and $P(O_2C_6H_4)$ centers. The decrease in coupling with increase in temperature can be explained on the basis of the earlier finding that the $^2J_{PP}$ for a conformer of type *a* is large and positive, whereas that for the conformer *c* or *d* is small and negative [6, 7]. An increasing proportion of the *a* type conformer would lead to numerically smaller coupling constant values. It is also likely that the conformer *d*

($X_2$ = ($O_2C_6H_4$), Y = Ph) with the lone pair on the P($O_2C_6H_4$) center cis to the N–C bond and the lone pair at $PPh_2$ center trans to the N–C bond may have a different $^2J_{PP}$ from the major conformer *c*. However, even at 195 K, no evidence for this conformer could be seen. The pair of doublets observed at $\delta$ 162.5 and 42.9 with a coupling of ~100 Hz is most likely to be due to conformer *a* [7].

### Crystal Structure Determination

The structure of the unsymmetrical diphosphazane **1** has been determined by single crystal X-ray diffraction. A perspective view of the two independent molecules in the unit cell is shown in Figure 3 [8]. The corresponding bond lengths and bond angles in the two molecules do not differ significantly. Selected bond lengths and bond angles are shown in Table 1. In Table 2, the structural data for compound **1** are compared with those observed for other diphosphazanes reported in the literature. As pointed out already, compound **1** adopts the conformation *c* in the solid state in which the electron pair on the diphenyl-substituted phosphorus is cis to the N–C bond and the electron pair on the *o*-phenylenedioxy-substituted phosphorus is trans to the N–C bond. The geometry around the phosphorus atoms and nitrogen atom are, respectively, trigonal pyramidal and almost planar. The same type of conformation is observed for the symmetrically substituted diphosphazane, $Ph_2PN(Pr^i)PPh_2$ in the solid state [7].

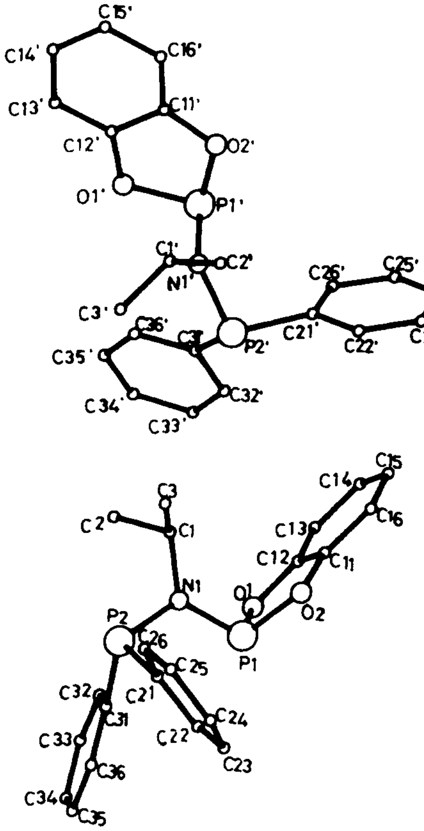


**FIGURE 3** PLUTO diagram of $Pr^iN(PPh_2)(PO_2C_6H_4)$ (**1**) showing the two independent molecules; carbon atoms are drawn with arbitrary radius for clarity.

**TABLE 1** Selected Bond Distances (Å) and Bond Angles (°) in $Pr^iN(PPh_2)(PO_2C_6H_4)$ (**1**)

| *Molecule 1* | | *Molecule 2* | |
|---|---|---|---|
| (*a*) *Bond Lengths* (*Å*) | | | |
| P1–N1 | 1.654(4) | P1′–N1′ | 1.655(3) |
| P1–O1 | 1.684(3) | P1′–O1′ | 1.699(4) |
| P1–O2 | 1.686(3) | P1′–O2′ | 1.685(3) |
| N1–C1 | 1.507(6) | N1′–C1′ | 1.500(8) |
| N1–P2 | 1.743(4) | N1′–P2′ | 1.739(3) |
| C1–C2 | 1.518(8) | C1′–C2′ | 1.532(7) |
| C1–C3 | 1.508(9) | C1′–C3′ | 1.506(8) |
| P2–C21 | 1.831(5) | P2′–C21′ | 1.830(7) |
| P2–C31 | 1.830(5) | P2′–C31′ | 1.834(5) |
| O1–C12 | 1.383(6) | O1′–C12′ | 1.373(7) |
| O2–C11 | 1.385(7) | O2′–C11′ | 1.376(8) |
| (*b*) *Bond Angles* (°) | | | |
| N1–P1–O1 | 103.4(2) | N1′–P1′–O1′ | 102.8(2) |
| N1–P1–O2 | 103.4(2) | N1′–P1′–O2′ | 103.3(2) |
| O1–P1–O2 | 92.0(2) | O1′–P1′–O2′ | 92.0(2) |
| P1–N1–C1 | 123.2(3) | P1′–N1′–C1′ | 122.9(3) |
| P1–N1–P2 | 120.7(2) | P1′–N1′–P2′ | 120.7(2) |
| C1–N1–P2 | 116.0(3) | C1′–N1′–P2′ | 116.4(3) |
| N1–C1–C2 | 110.6(5) | N1′–C1′–C2′ | 110.1(5) |
| N1–C1–C3 | 111.6(5) | N1′–C1′–C3′ | 112.6(5) |
| C2–C1–C3 | 111.8(5) | C2′–C1′–C3′ | 112.1(5) |
| N1–P2–C21 | 104.7(2) | N1′–P2′–C21′ | 105.3(2) |
| N1–P2–C31 | 102.9(2) | N1′–P2′–C31′ | 103.4(2) |
| C21–P2–C31 | 103.8(2) | C21′–P2′–C31′ | 103.3(3) |
| P1–O1–C12 | 111.4(3) | P1′–O1′–C12′ | 111.4(3) |
| P1–O2–C11 | 111.5(3) | P1′–O2′–C11′ | 111.0(3) |

Two different P–N bond lengths are observed for compound **1**; the P(1)–N(1) bond length (1.654(4) Å) connecting the *o*-phenylenedioxy-substituted phosphorus is shorter than the P(2)–N(1) bond length (1.743(4) Å) involving the phenyl-substituted phosphorus center. This difference presumably arises as a result of the increased $\pi$-bonding in the P(1)–N(1) segment owing to the increased electron-withdrawing effect of the *o*-phenylenedioxy group. The P–N–P angle is 120.7(2)°.

In general, the P–N bond lengths for the symmetrically substituted diphosphazanes reported in the literature (Table 2) lie in the range 1.67–1.70 Å and the P–N–P angles lie in the range 110–123°.

## EXPERIMENTAL

All operations were carried out under an atmosphere of pure and dry dinitrogen. Toluene and tetrahydrofuran were distilled and stored over sodium wire. $ClP(O_2C_6H_4)$ and $Ph_2P(NHPr^i)$ were

**TABLE 2** Structural Data for Diphosphinoamines Obtained from X-ray Diffraction Studies

| *Compound* | *Conformer* | *P–N–P(°)* | *P–N(Å)* | *P··P(Å)* | *Ref.* |
|---|---|---|---|---|---|
| $(PF_2)_2NH$ | $C_{2v}$ | 120.7(4)<br>122.1(7) | 1.667(10)<br>1.684(8) | 2.893(3)<br>2.948(14) | [9][a]<br>[14][b] |
| $(PF_2)_2NMe$ | $C_{2v}$ | 116.1(8) | 1.680(6) | 2.851(10) | [10][b] |
| $(PCl_2)_2NMe$ | $C_{2v}$ | 117.4(3) | 1.661(10) | 2.838(10) | [11][c] |
| $((PCl_2)_2NPh$ | $C_{2v}$ | 110.8(8) | 1.69(3) | — | [13] |
| $\{P(NHPh)\}_2NPh$ | $C_{2v}$ | 117.7(5) | 1.67(1)<br>1.71(1) | 2.897(6) | [12] |
| $(PPh_2)_2NPr^i$ | $C_s$ | 122.8(3) | 1.706(4)<br>1.711(4) | 3.001(2) | [7] |
| $Pr^iN(PPh_2)$ $P(O_2C_6H_4)$ | $C_s$ | 120.7(2) | 1.654(4) (P(1)–N(1))<br>1.743(4) (N(1)–P(2)) | 2.953(3) | This work |

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[a] Structure determined at 163 K.

[b] Structure determined by electron diffraction in the gas phase.

[c] Obtained from NMR studies of a sample partially oriented in a Nematic liquid crystal.

prepared by literature methods [15, 16]; $PPh_2Cl$ (Aldrich) was used as supplied.

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer; the $^1H$ and $^{13}C$ NMR spectra were obtained using a Bruker WH270 spectrometer. The $^{31}P\{^1H\}$ spectra were recorded on a Varian FT-80A (32.2 MHz) and a Bruker ACF200 (80.1 MHz) spectrometer. Proton and $^{13}C$ chemical shifts are referred to tetramethylsilane (0.0) as the internal standard, while $^{31}P$ shifts are quoted with reference to 85% $H_3PO_4$ (0.0) as an external standard. Elemental analyses were obtained from the City University, London.

### (*Diphenylphosphino*)-(o-*phenylenedioxyphosphino*)-*isopropylamine* (**1**)

A solution of $ClP(O_2C_6H_4)$ (0.05 mol, 8.72 g) in toluene (40 mL) was added dropwise to (isopropylamino)diphenylphosphine (0.05 mol, 12.15 g) and triethylamine (0.055 mol, 5.55 g) in toluene (40 mL) at 0°C. The mixture was stirred for 1 h; the colorless precipitate of triethylamine hydrochloride (0.042 mol, 5.77 g) was removed by filtration and washed with toluene (50 mL). The pale brown filtrate was reduced to half its volume in vacuo and the solution was passed through a silica gel column. Solvent was removed in vacuo from the eluent to obtain a colorless solid; recrystallization of the solid from toluene–petroleum ether mixture (1:4) gave colorless prismatic crystals: yield 15.62 g (82%), mp 82–83°C. Anal. Calcd. for $C_{21}H_{21}NO_2P_2$: C, 66.08; H, 5.56; N, 3.67. Found: C, 66.24; H, 5.52; N, 3.62. IR (Nujol mull): 1220(s), 1000(m), 880(m), 810(s), 730(s), 680(m). $^1H$ NMR ($CDCl_3$): $\delta$ 7.6–7.3 (10H, m, Ph), 7.0–6.83 (4H, m, Ph), 3.4 (1H, septet, CH, $^3J_{HH}$ = 6.6 Hz), 1.2 (6H, d, $CH_3$, $^3J_{HH}$ = 6.5 Hz). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$): $\delta$ 155.8 (d), 28.9 (d) ($^2J_{PP}$ = 14 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 147.4 (d, $^2J_{PC}$ = 7.2 Hz, 1,6 carbons of dioxyphenyl group), 138.9 (dd, $J_{PC}$ = 14.2 and 10.2 Hz, *ipso* carbons of Ph), 132 (m, Ph), 128 (m, Ph), 121.8 (s, 2,5 carbons of dioxyphenyl group), 111.6 (s, 3,4 carbons of dioxyphenyl group), 47.2 (d, $J_{PC}$ = 21.8 Hz, CH), 23.9 (d, $J_{PC}$ = 11.6 Hz, $CH_3$).

### (*Isopropylamino*)(o-*phenylenedioxy*)-*phosphine* (**2**)

A solution of $ClP(O_2C_6H_4)$ (0.05 mol, 8.72 g) in toluene (40 mL) was added dropwise to isopropylamine (0.11 mol, 6.49 g) in toluene (40 mL) at 0°C. The mixture was stirred for 30 minutes; the colorless precipitate of isopropylamine hydrochloride (4.15 g) was removed by filtration and washed with toluene (60 mL). The filtrate was evaporated under reduced pressure (1 mmHg) at room temperature to give a pale brown oil that was highly air-sensitive and had an unpleasant smell: yield 87%. IR (neat): 3350(m), 2950(m), 1480(s), 1240(s), 1130(m), 1020(m), 820(s), 740(m). $^1H$ NMR ($CDCl_3$): $\delta$ 7.1 (4H, m, Ph), 3.26 (1H, septet, CH, $^3J_{HH}$ = 6.3 Hz), 1.46 (1H, d, NH, $^2J_{PH}$ = 6.2 Hz), 1.1 (6H, d, $CH_3$, $^3J_{HH}$ = 6.3 Hz). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$): $\delta$ 139.5 (s).

### *Bis*-(o-*phenylenedioxyphosphino*)-*isopropylamine* (**3**)

A solution of $ClP(O_2C_6H_4)$ (0.04 mol, 6.98 g) in tetrahydrofuran (40 mL) was added dropwise to compound **2** (0.04 mol, 7.88 g) and triethylamine (0.044 mol, 4.44 g) in tetrahydrofuran (40 mL) at 0°C. The mixture was stirred for 1 h; the colorless precipitate of triethylamine hydrochloride (4.73 g) was filtered off and the filtrate was evaporated in

**TABLE 3** Crystal Data and Intensity Collection Parameters for $Pr^iN(PPh_2)(PO_2C_6H_4)$ (**1**)

| | |
|---|---|
| Formula | $C_{21}H_{21}NO_2P_2$ |
| Molecular weight | 381.33 |
| Crystal system | Monoclinic |
| Space group | *C*2/*c* |
| *Z* | 16 |
| *a*, Å | 34.149(5) |
| *b*, Å | 9.717(6) |
| *c*, Å | 29.439(5) |
| *β*, ° | 125.11(2) |
| *V*, Å$^3$ | 7991.36 |
| Crystal dimensions, mm | 0.38 × 0.30 × 0.22 |
| $d_m$, gcm$^{-3}$ | 1.25 |
| $d_c$, gcm$^{-3}$ | 1.27 |
| *F*(000), | 3200.00 |
| Radiation (graphite monochromator) | Mo-K$\alpha$ (0.71069 Å) |
| Linear abs. coeff. $\mu$cm$^{-1}$ | 1.88 |
| Scan technique | $\omega/2\theta$ |
| $\theta$ range | 1–25 |
| Total no. of reflections | 7658 |
| Unique reflections | 7003 |
| Observed reflections | 4094 [$Fo > 5.0\ \sigma\ (Fo)$] |
| *R* | 0.0581 |
| $R_w$ | 0.0612 |
| Largest peak in final diff. map, e/Å$^3$ | 0.298 |
| $(\Delta/\sigma)_{\max}$ | 0.165 |

$R = (||Fo| - |Fc||)/\Sigma|Fo|$; $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$, $w = 2.1695/(\sigma^2(Fo) + 0.00001\ (Fo)^2)$.

vacuo to give a pale yellow viscous liquid. This was purified by dissolving it in tetrahydrofuran–petroleum ether mixture (1 : 1) and passing the solution through a silica gel column. Solvent was removed in vacuo from the eluent and a colorless air-sensitive deliquescent solid was obtained. The crude product was recrystallized from ethyl acetate: yield 9.92 g (74%), mp 91–92°C. Anal. Calcd. for $C_{15}H_{15}NO_4P_2$: C, 53.74; H, 4.52; N, 4.18. Found: C, 52.36; H, 4.73; N, 4.28. IR (Nujol mull): 1220(s), 1020(m), 800(s), 740(s), 720(s). $^1H$ NMR ($CDCl_3$): $\delta$ 7.2–6.9 (8H, m, Ph), 3.3–3.2 (1H, septet, CH, $^3J_{HH}$ = 6.7 Hz), 1.2 (6H, d, $CH_3$, $^3J_{HH}$ = 6.7 Hz). $^{31}P\{^1H\}$ NMR ($CHCl_3$): 149.9 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 146.4 (s, 1,6 carbons of dioxyphenyl groups), 122.6 (s, 2,5 carbons of dioxyphenyl groups), 112.2 (s, 3,4 carbons of dioxyphenyl groups, 47.4 (s, CH), 25.0 (s, $2CH_3$).

## *CRYSTAL STRUCTURE DETERMINATION*

A summary of the crystal data for compound **1** and parameters pertinent to the structure determination are given in Table 3. The crystal was coated with an epoxy glue to protect it from atmosphere during data collection. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation. Cell constants were obtained by least-squares refinement of the setting angles of 21 reflections in the

**TABLE 4** Nonhydrogen Atomic Coordinates and Isotropic Thermal Parameters (Å$^2$ × 10$^4$) for $Pr^iN(PPh_2)(PO_2C_6H_4)$ (**1**)

| *Atom* | *x*/*a* | *y*/*b* | *z*/*c* | $U_{eq}$ |
|---|---|---|---|---|
| *Molecule 1* | | | | |
| P1 | 0.10147(4) | 0.14876(15) | 0.15693(5) | 533(5) |
| N1 | 0.0693(1) | 0.1477(4) | 0.1827(1) | 457(11) |
| C1 | 0.0842(2) | 0.0715(5) | 0.2349(2) | 513(12) |
| C2 | 0.0909(2) | 0.1707(6) | 0.2787(2) | 801(13) |
| C3 | 0.0495(2) | −0.0419(5) | 0.2233(2) | 777(13) |
| P2 | 0.01358(4) | 0.22785(13) | 0.14748(5) | 435(5) |
| O1 | 0.1568(1) | 0.1889(3) | 0.2121(1) | 548(10) |
| O2 | 0.1163(1) | −0.0180(3) | 0.1597(1) | 593(10) |
| C11 | 0.1623(2) | −0.0443(5) | 0.2058(2) | 493(12) |
| C12 | 0.1853(2) | 0.0730(5) | 0.2349(2) | 472(12) |
| C13 | 0.2312(2) | 0.0707(5) | 0.2815(2) | 588(12) |
| C14 | 0.2537(2) | −0.0531(6) | 0.2982(2) | 716(13) |
| C15 | 0.2313(2) | −0.1746(6) | 0.2697(2) | 709(12) |
| C16 | 0.1847(2) | −0.1713(5) | 0.2223(2) | 664(13) |
| C21 | −0.0217(1) | 0.1420(4) | 0.0798(2) | 428(12) |
| C22 | −0.0555(2) | 0.0487(5) | 0.0727(2) | 573(12) |
| C23 | −0.0840(2) | −0.0255(5) | 0.0242(2) | 697(12) |
| C24 | −0.0789(2) | −0.0036(5) | −0.0187(2) | 615(12) |
| C25 | −0.0455(2) | 0.0878(5) | −0.0126(2) | 583(12) |
| C26 | −0.0170(2) | 0.1602(5) | 0.0364(2) | 501(12) |
| C31 | 0.0258(2) | 0.3980(4) | 0.1317(2) | 454(12) |
| C32 | 0.0653(2) | 0.4707(5) | 0.1739(2) | 646(12) |
| C33 | 0.0723(2) | 0.6065(6) | 0.1668(2) | 745(13) |
| C34 | 0.0405(2) | 0.6742(5) | 0.1185(2) | 719(13) |

**TABLE 4** (*continued*)

| *Atom* | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| C35 | 0.0015(2) | 0.6043(5) | 0.0761(2) | 696(13) |
| C36 | −0.0061(2) | 0.4676(5) | 0.0829(2) | 562(12) |
| *Molecule 2* | | | | |
| P1′ | 0.18125(5) | −0.38721(15) | 0.46728(5) | 559(6) |
| N1′ | 0.1371(1) | −0.3670(4) | 0.4009(1) | 483(11) |
| C1′ | 0.0871(2) | −0.4163(5) | 0.3763(2) | 548(12) |
| C2′ | 0.0755(2) | −0.5392(6) | 0.3379(2) | 891(13) |
| C3′ | 0.0505(2) | −0.3032(6) | 0.3476(2) | 849(13) |
| P2′ | 0.14728(4) | −0.28834(13) | 0.35556(5) | 472(5) |
| O1′ | 0.1587(1) | −0.3147(3) | 0.5002(1) | 584(11) |
| O2′ | 0.1722(1) | −0.5474(3) | 0.4814(1) | 643(11) |
| C11′ | 0.1539(2) | −0.5436(5) | 0.5126(2) | 553(12) |
| C12′ | 0.1462(2) | −0.4129(5) | 0.5232(2) | 514(12) |
| C13′ | 0.1280(2) | −0.3884(5) | 0.5536(2) | 660(12) |
| C14′ | 0.1186(2) | −0.5026(7) | 0.5746(2) | 787(13) |
| C15′ | 0.1265(2) | −0.6331(6) | 0.5646(2) | 823(13) |
| C16′ | 0.1435(2) | −0.6558(5) | 0.5330(2) | 739(13) |
| C21′ | 0.1966(2) | −0.3844(5) | 0.3628(2) | 478(12) |
| C22′ | 0.1848(2) | −0.4701(5) | 0.3192(2) | 673(12) |
| C23′ | 0.2186(2) | −0.5454(6) | 0.3187(2) | 876(13) |
| C24′ | 0.2654(2) | −0.5350(6) | 0.3617(2) | 773(13) |
| C25′ | 0.2779(2) | −0.4510(7) | 0.4052(2) | 857(13) |
| C26′ | 0.2441(2) | −0.3770(6) | 0.4060(2) | 711(13) |
| C31′ | 0.1749(2) | −0.1238(5) | 0.3896(2) | 483(12) |
| C32′ | 0.2021(2) | −0.0538(5) | 0.3756(2) | 635(12) |
| C33′ | 0.2174(2) | 0.0794(6) | 0.3944(2) | 742(13) |
| C34′ | 0.2063(2) | 0.1448(5) | 0.4270(2) | 729(13) |
| C35′ | 0.1795(2) | 0.0774(6) | 0.4402(2) | 789(13) |
| C36′ | 0.1634(2) | −0.0555(5) | 0.4215(2) | 635(12) |

$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \vec{a}_i\vec{a}_j$.

range $7.9 < \theta < 16.3$. In the course of the data collection, no decrease in intensity was observed as monitored by three repeatedly measured control reflections. Lorenz-Lorentz polarization corrections were applied to the intensity data, but no absorption correction was made because of the low absorption coefficient.

The structure was solved by direct methods using SHELXS-86 [17] program and least square refinements were performed by the full-matrix method with SHELX-76 [18]. All hydrogens were located from difference Fourier maps. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Nonhydrogen atom coordinates are given in Table 4.

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