Conformations of Diphosphinoamines; Variable-temperature Nuclear Magnetic Resonance and *X*-Ray Crystallographic Studies

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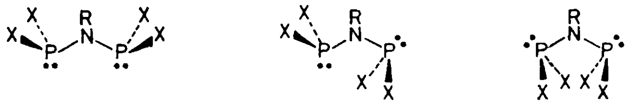
The variable-temperature $^{31}P-\{^1H\}$ n.m.r. spectra of a series of diphosphinoamines, $X_2PN(R)PX_2$ (R = H, Me, Et, or Pr^i, X = Ph; R = Me, Bu^t, or CH$_2$Bu^t, X = Cl; R = Me or Bu^t, X = F; R = Et, X = NMe$_2$) have been studied. Complementary information on these compounds has been obtained from ^{1}H, ^{13}C, and ^{19}F n.m.r., including double and triple resonance experiments. The coupling constant, $^2J(PNP)$, covers the range −23.9 to 731.9 Hz, and its magnitude and sign can be related to the proportion of molecules in which the local symmetry of the P–N–P skeleton is C_{2v} rather than C_s. Diphosphinoamine conformers of the latter type have been clearly identified for the first time both in solution (for R = Et or Pr^i, X = Ph, and R = Bu^t or CH$_2$Bu^t, X = Cl) and also in the solid phase. *X*-Ray analysis of Ph$_2$PN(Pr^i)PPh$_2$, based on 1 269 diffractometric intensities refined to R = 0.035, shows that the symmetry of the P–N–P skeleton is close to C_s in the solid, with P–N = 1.706(4) and 1.711(4) Å, and PNP = 122.8(3)°.

THE conformations of the diphosphinoamines, $X_2PN(R)PX_2$ (R = alkyl, X = alkoxy, amino, halogeno, or phenyl) have recently attracted considerable interest. Their n.m.r. spectra [1–9] have thrown light on this topic, and particular attention has been centred on the spin coupling constant $^2J(PNP)$, which can assume an extraordinarily wide range of values (−35 to 665 Hz).[5,6] The possibility that this coupling may be correlated with the relative proportions of the conformers shown below has been considered (the point group symbols refer to the local symmetry of the P–N–P skeleton and do not take account of the conformations of X and/or R groups). It is generally thought that conformations of the type C_{2v}' would suffer severe steric interactions and hence do not play a significant part in any conformational equilibrium.



C_{2V} C_S C_{2V}'

In the vapour phase, (1b) (R = Me, X = F) adopts the C_{2v} conformation,[10] and only slight deviations from this symmetry are found [11] for 72% of (1a) (R = H, X = F) at ambient temperature. A second conformer of (1a), identified in the same study, is derived from the C_{2v} arrangement by twisting one PF$_2$ group by 60° about the adjacent P–N bond. In the solid state (1a) [12] has a C_{2v} skeletal conformation, and (5) [R = Ph, X$_2$ = (NPh)$_2$PNHPh] [13] appears from a figure to be similar. The *exo*-PNP skeleton of [(Ph$_2$PNMe)PNBu^t]$_2$ also has a conformation analogous to C_{2v}.[14] All four structural investigations showed that the bridging nitrogen atom has a planar distribution of bonds. The C_{2v} conformation has been associated with large positive *PNP* spin couplings,[5–8] although discussion of substituent effects is fraught with uncertainties regarding the relative proportions of other conformers. Of the three molecules known to crystallise as C_{2v}-type conformers only [(Ph$_2$PNMe)PNBu^t]$_2$ displays a relatively large *PNP* coupling; [14] an intermediate value is found for (1a) (±154 Hz),[4] while for (5) the *PNP* coupling is reported to be as low as ±3 Hz.[13] We now report on a variable-temperature n.m.r. study of a series of diphosphinoamines which provides new insight into the conformers present in solution. A further indication that solid-state structures and preferred conformations in solution are closely related now comes from an *X*-ray crystallographic study of (2d) (R = Pr^i, X = Ph).

RESULTS AND DISCUSSION

The $^{31}P-\{^1H\}$ n.m.r. data, mainly obtained at sub-ambient temperatures, are summarised in Table 1. An increase in $|^2J(PNP)|$ as the temperature is lowered has been noted for the fluorides [R = Me (1b), Et (1c),[2,3] and SiH$_3$ (1f) [8]] with the greatest temperature dependence (−0.7 Hz K^{-1}) for the silyl compound.[8] We now find that for (1b) (R = Me, X = F), $J(PNP)$ reaches a limiting value (443 Hz) at *ca.* −60 °C (*cf.* ref. 3). The ^{31}P n.m.r. spectrum is broad at ambient temperatures (*cf.* Figure 1) because of ^{14}N spin coupling which is incompletely collapsed by ^{14}N quadrupolar relaxation. At lower temperatures the quadrupolar relaxation is more efficient and loss of the ^{14}N coupling gives sharper ^{31}P lines; at higher temperatures the quadrupolar relaxation is less efficient and at 80 °C the ^{31}P spectrum is again sharper but also displays a triplet splitting arising from $^1J(^{31}P-^{14}N)$ = 43 Hz.

Compound (1e) (R = Bu^t, X = F) also gives a ^{31}P spectrum corresponding to the AA′ part of an $X_2AA'X'_2$ spin system and at temperatures above *ca.* −80 °C was also found to have a temperature dependent $J(PNP)$ (maximum variation *ca.* −2.3 Hz K^{-1}) and show similar linewidth behaviour to the methyl compound. However below *ca.* −80 °C the spectrum broadens again (Figure 1), and then resharpens at *ca.* −110 °C to give another spectrum of an $X_2AA'X'_2$ system with a large temperature-invariant $J(PNP)$ of 732 Hz (to the best of our knowledge, the largest known P···P coupling involving tervalent phosphorus). This type of linewidth/temperature behaviour is characteristic of the

TABLE 1

^{31}P N.m.r. data for diphosphinoamines, $X_2PN(R)PX_2$

Compound	δ (P)	$\lvert J(PNP)\rvert$/Hz	Solvent	θ_C/°C
(1b) (R = Me, X = F) [a]	141.7	434.7	Neat +20% C_6D_6–$SiMe_4$	Ambient
	140.8	443.1		−70
(1e) (R = Bu^t, X = F) [b]	157.7	348	CD_2Cl_2–$CFCl_3$	Ambient
	154.0	731.9	CD_2Cl_2–$CFCl_3$	−125
(3c) (R = Et, X = Cl)	163.0 [c]		$CDCl_3$–CD_2Cl_2	−110
(3e) (R = Bu^t, X = Cl)	170.0		$CDCl_3$	5
	175.0, 163.7	20.1	$CDCl_3$	−70
(3g) (R = CH_2Bu^t, X = Cl) [d]	171.7		CD_2Cl_2–$CFCl_3$ (1 : 1)	Ambient
	172.0, 167.6	17.9	CD_2Cl_2–$CFCl_3$ (1 : 1)	−130
(2a) (R = H, X = Ph) [e]	42.6	166	Toluene–$CDCl_3$ (2 : 1)	0
	42.8	185	Toluene–$CDCl_3$ (2 : 1)	−60
(2b) (R = Me, X = Ph)	74.0	*f*	$CDCl_3$–CD_2Cl_2	−110
(2c) (R = Et, X = Ph)	62.2		$CDCl_3$	Ambient
	68.2, 51.8 75.1	22.4	$CDCl_3$–CD_2Cl_2 (1 : 1)	−100
(2d) (R = Pr^i, X = Ph) [g]	48.8		$CDCl_3$	Ambient
	52.9, 39.6	23.9	$CDCl_3$	−60
(5) [R = Ph, X_2 = $(NPh)_2PNHPh$]	108.0		$CDCl_3$	Ambient
	105.6		$CDCl_3$	−60
(4c) (R = Et, X = NMe_2)	121.3		CD_2Cl_2	Ambient
	127, 119, 111, 97 (*ca.* 1 : 2 : 2 : 1)		CD_2Cl_2–$CHFCl_2$ (1 : 1)	*ca.* −150

[a] $\lvert ^1J(P^{14}N)\rvert$ = 43 Hz at 80 °C. In the vapour phase the ^{19}F spectrum is a broad doublet δ(F) −82, ^1J(PF) *ca.* 1.160 Hz, $W_{\frac{1}{2}}$ *ca.* 300 Hz, see refs. 1—3 for solution-phase ^{19}F n.m.r. [b] ^{19}F n.m.r. (ambient temperature): δ(F) −64.7, ^1J(PF) −1 271.6, ^3J(PF′) 76.0, $\lvert ^4J(FF')\rvert$ 20.5, 11.0 Hz. ^{19}F n.m.r. (−125 °C): δ(F) −64.8, ^1J(PF) −1 287.9, ^3J(PF′) 109.2 Hz. [c] Width at half peak height *ca.* 70 Hz. [d] ^{1}H n.m.r.: δ(CH_2) 3.46, ^3J(PH) 14.7 Hz; δ(CH_3) 1.06. [e] ^{1}H n.m.r.: δ(NH) 3.20, $^2J(PNH)$ 3.8 Hz [opposite sign to $J(PNP)$] at 0 °C [$^2J(PNH)$ increases to 5.2 Hz at −60 °C]. [f] ^1H-{^{31}P} double resonance showed that $J(PNP)$ is 284 Hz at 25°C and 302 Hz at −40 °C. [g] ^{1}H n.m.r.: (ambient temp.) δ(CH_3) 1.10, J(HCCH) 6 Hz, δ(CH) 3.72, J(PNCH) 12 Hz; (−65 °C) J(PNCH) *ca.* 18 and 4 Hz.

exchange broadening shown by an equilibrium involving a minor component,[15] but the complexity of the spectra makes it very difficult to obtain an estimate of the rate of exchange. At temperatures below −120 °C, some new broad signals (*ca.* 5%) were visible but could not be analysed. Related behaviour was observed in the ^{19}F n.m.r. spectra.

In the case of the chloride (3e) (R = Bu^t, X = Cl), the ^{31}P spectrum was a singlet at ambient temperatures, but formed two spin-coupled doublets (AB system) below −60 °C, where $^2J(PNP)$ was temperature-invariant. Similar behaviour was observed for (3g) (R = CH_2Bu^t, X = Cl), for (2d) (Figure 2), and for the analogous ethyl compound (2c) (R = Et, X = Ph), although in the latter case the two doublets accounted for only 83% of the total spectrum, the remainder being a singlet. The ^{31}P-{^{1}H} n.m.r. spectra of (3b, c) (R = Me or Et, X = Cl), (2a, b) (R = H or Me, X = Ph), and of (4c) (R = Et, X = NMe_2) all consisted of a singlet at temperatures down to −100 °C. The latter compound gave four broad signals ($W_{\frac{1}{2}}$ = *ca.* 250 Hz) at the lowest temperature attainable, *ca.* −150 °C (Table 1), but this observation is not understood. The temperature dependence of $^2J(PNP)$ in (2a, b) was followed by ^{1}H-{^{31}P} double resonance as previously employed.[5,6]

Changes in the multiplicity of the ^{31}P signals can be interpreted in terms of restricted rotation about the P–N bonds. The appearance of two spin-coupled doublets at low temperatures indicates the presence of conformers with C_s symmetry. Although the free energies of activation for the rate processes have not been measured, they must generally be in the range 9—11 kcal mol^{-1} * at −100 to −50 °C; P^{III}–N torsional barriers of this magnitude are well established.[16,17] No evidence has been obtained for a C_{2v}' conformer. Generally, C_s conformers arise with relatively bulky R groups as might be expected, and these conformers are remarkable for the relative constancy of $J(PNP)$ considering that there are large differences in the electronegativity of the X groups. By contrast, the low-temperature forms of (1b, e) (R = Me and Bu^t, X = F), both presumably with C_{2v} symmetry, have a difference in $J(PNP)$ of *ca.* 300 Hz. This difference may arise from a steric effect of R on the P–N–P angle, and a relationship between the coupling and the proximity of the phosphorus lone pairs (see below). However, we conclude that changes in $J(PNP)$ with temperature for a given diphosphinoamine are largely a reflection of the relative proportions of C_{2v} and C_s conformers. The temperature dependence of $J(PNP)$ for (1e) is shown in Figure 3. The region where this coupling becomes independent of temperature corresponds to the observation of the spectrum of a single (C_{2v}) conformer. If the C_{2v}' conformer is absent, then the limiting coupling at high temperatures will be $\frac{1}{3}J(C_{2v}) + \frac{2}{3}J(C_s)$ (the latter conformer has twice the population of the former conformer on statistical grounds). If the further assumption that $J(C_s)$ = −20 Hz is made (for sign information see below), then for (1e) where $J(C_{2v})$ = 732 Hz it can be calculated that $J(PNP)$ at elevated temperatures will be 231 Hz. This

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* Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

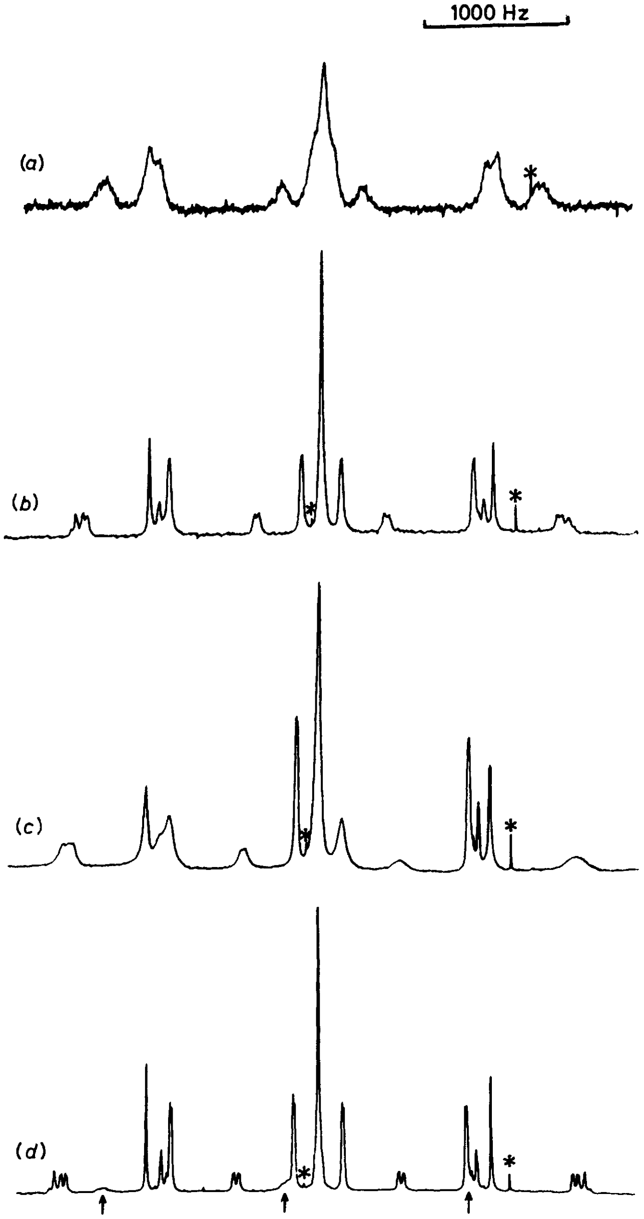

FIGURE 1 The ^{31}P-{^{1}H} spectra of (1e) (R = Bu^{t}, X = F) obtained at various temperatures: (*a*) ambient; (*b*) −60; (*c*) −100; (*d*), −125 °C (the frequency increases from right to left). The spectra have slightly different offsets to align the central peaks of the spectra. The broad peaks arrowed in the −125 °C spectrum are attributed to a minor conformer. Impurity peaks are marked with an asterisk

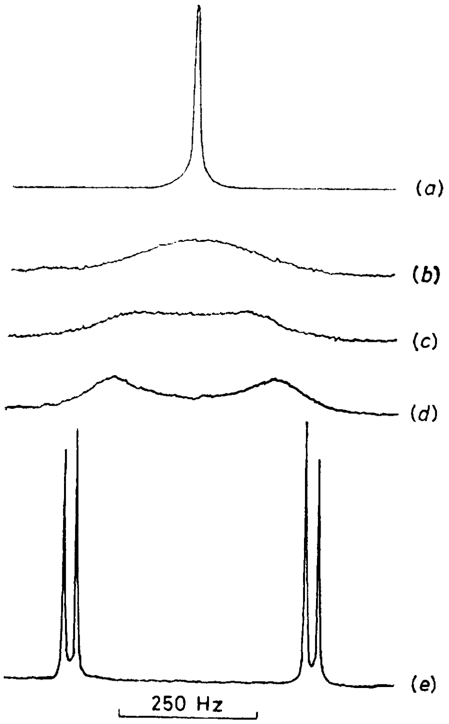

FIGURE 2 Variable-temperature ^{31}P-{^{1}H} n.m.r. spectra of (2d) (R = Pr^{i}, X = Ph): (*a*) 25; (*b*) 10; (*c*) 5; (*d*) 0; and (*e*) −60 °C

compares well with the trend observed up to 67 °C, where this coupling (314.6 Hz) has not yet reached a temperature-independent value.

Similar assumptions can be made to estimate the relative proportions of C_{2v} and C_s conformers in (1b, e) at ambient temperatures, which will be given by $J(\text{observed}) = pJ(C_{2v}) + (1 - p)J(C_s)$, where p is the fractional population of the C_{2v} conformer. This fraction is *ca.* 1 and 0.5 for R = Me and Bu^{t} respectively. An analysis [10] of the electron diffraction data for (1b) showed that the major conformer has the C_{2v} conformation but that the presence of $\leqslant 15\%$ of the C_s conformer could not be ruled out. The vapour-phase ^{19}F n.m.r.

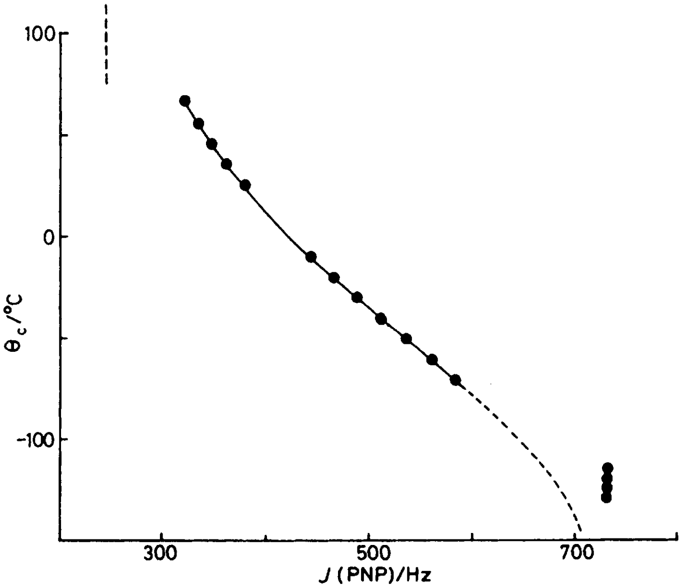

FIGURE 3 Graph showing the temperature dependence of $J(PNP)$ in (1e) (R = Bu^{t}, X = F) (obtained from the ^{19}F n.m.r. spectra, solvent CD_2Cl_2–$CFCl_3$). The experimental data are in two regions, shown by the continuous lines. The vertical broken line at high temperature indicates the coupling constant expected for a statistical mixture of C_{2v} and C_s isomers. The broken line at low temperature indicates the coupling constant that would be expected if conformational interchange remained rapid on the n.m.r. time scale

spectrum of (1b) was too broad to obtain *PNP* coupling information. Limiting *PNP* couplings for the C_{2v} conformers of (2b, c, d) (R = Me, Et, or Pr^i, X = Ph) are difficult to obtain. Hydrogen-1-{^{31}P} double resonance experiments gave a *PNP* coupling for the methyl compound of 302 Hz at −40 °C, which is probably close to the limiting value. Even if $J(PNP)$ for the C_{2v} conformer is as large as 350 Hz, then the fractional population, *p*, for the C_{2v} conformer at ambient temperatures would be *ca.* 0.8. The small *PNP* coupling (<50 Hz) [5] in the analogous ethyl compound indicates that the C_s conformer predominates at ambient temperatures as well as at −100 °C (Table 1).

Low-temperature ^{1}H n.m.r. spectroscopy did not generally prove very useful for the identification of C_{2v} and/or C_s conformers, mainly because of the complexity of the signals. The C_s conformer of (2d) did, however, show different *PNCH* couplings (Table 2) after ^{1}H-{^{1}H} homonuclear decoupling of the methyl protons.

TABLE 2

^{13}C N.m.r. data [a]

Compound	δ(N*C*)	*J*(PNC)/Hz	θ$_c$/°C	Other data	
(3e)	70.1	13.3	Ambient	δ(PNC*C*) *J*(PNC*C*)	31.8 8.6 Hz
	69.8	26.2 [b] <0.5	−60	δ(PNC*C*) *J*(PNC*C*)	31.6 [c] *d*
(2d)	51.9	10.0	Ambient	See ref. 18	
	52.0	−7.1 [b] 27.0	−60		

[a] $CDCl_3$ solutions. [b] Coupling to low-field phosphorus. [c] Triplet with broad central peak. [d] Sum of couplings to both ^{31}P nuclei = 16.3 Hz.

Information on the sign of $J(PNP)$ in the C_s conformer of (2d) was obtained from ^{13}C-{^{31}P, $^1H_{noise}$} triple resonance experiments. The methine-carbon signal at −60 °C was a doublet of doublets (Table 2). Phosphorus-31 irradiation showed that $J(PNC) = \pm 27.0$, ∓ 7.1 Hz, and $J(PNP) = \mp 23.9$ Hz. No *PNC* couplings less than −12 Hz have been identified,[18] so that $J(PNP)$ is negative as in $Ph_2PN(Pr^i)PPhCl$ (−29 Hz at ambient temperature).[5] These experiments also established that the high-field ^{31}P signal arises from the phosphorus atom with its lone pair in a *cis* position with respect to the isopropyl group (*cf.* ref. 18). The methyl carbons are equivalent at both high and low temperature suggesting that the P–N–P skeleton lies on a plane of mirror symmetry as expected for a C_s conformer. The sign of $J(PNP)$ in (3e) was not established because only one *PNC* coupling was detectable, but it was shown that the low-field ^{31}P signal arises from the phosphorus atom with its lone pair *cis* to the t-butyl group.

The finding that the low-field ^{31}P signal in (3e) is associated with the phosphorus atom with a lone pair *cis* to the t-butyl group is consistent with the low-field shift induced by increasingly bulky R groups in the series (3) ($R = Me^1 \longrightarrow Et^1 \longrightarrow CH_2Bu^t \sim Bu^t$; X = Cl) at ambient temperatures. The same trend is apparent with the analogous fluorides, and can be related to increasing proportions of the C_s conformers in both series. The opposite phosphorus lone pair–^{31}P shift relationship for (2d) is in accord with the upfield shift that accompanies increasing bulk of the R group in the compounds $X_2PN(R)PX_2$ (R = alkyl, X = Ph). The *PNP* coupling constant data rule out the possibility of a tautomerisation of the type $X_2PN(R)PX_2 \rightleftharpoons X_2P(=NR)PX_2$, which is known [19] to occur with bulky X groups. Thus $^1J(PP)$ in compounds of the type $X_2P(=NR)PX_2$ is generally in the range 250—300 Hz. However, it is worth noting that attempts to prepare (2e) (R = Bu^t, X = Ph) resulted in the formation of tetraphenyldiphosphine oxide, $Ph_2PP(O)Ph_2$, which would be a probable hydrolysis product of $Ph_2PP(=NR)Ph_2$ (R = Bu^t).

The foregoing conclusions regarding the conformation of (2d) in solution are reinforced by the results of a single-crystal *X*-ray diffraction study (see Figure 4 and Table 3). The crystals contain well separated $Ph_2PN(Pr^i)PPh_2$ molecules of the C_s conformeric type, with the lone pairs of phosphorus atoms P(1) and P(2) approximately *trans* and *cis* respectively to the N–C(isopropyl) bond. Deviations of the central P–N–P skeleton from exact mirror symmetry are minor; the most notable are (*i*) distortions of the bonds at nitrogen from coplanarity [the maximum deviation of any of the

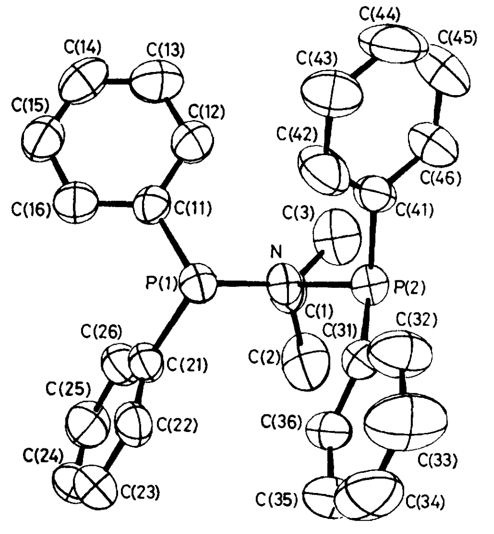

FIGURE 4 The $Ph_2PN(Pr^i)PPh_2$ (2d) molecule viewed along the direction of the N–C (isopropyl) bond. Hydrogen atoms are omitted and 50% probability ellipsoids are displayed

TABLE 3

Selected distances and angles in $Ph_2PN(Pr^i)PPh_2$ (2d)

(*a*) Bond lengths (Å)

P(1)–N	1.706(4)	C(11)–P(1)	1.833(5)
P(2)–N	1.711(4)	C(21)–P(1)	1.848(7)
C(1)–N	1.511(8)	C(31)–P(2)	1.819(6)
C(2)–C(1)	1.513(14)	C(41)–P(2)	1.847(6)
C(3)–C(1)	1.514(14)		
C–C (phenyl)	1.315(18)—1.401(12)	Mean 1.365(5)	
C–H	0.75(7) —1.07(6)	Mean 0.93(2)	

(*b*) Bond angles (°)

N–P(1)–C(11)	102.9(3)	N–C(1)–C(3)	112.6(6)
N–P(1)–C(21)	106.4(2)	C(2)–C(1)–C(3)	111.1(8)
C(11)–P(1)–C(21)	101.9(3)	P(1)–C(11)–C(12)	119.3(5)
N–P(2)–C(31)	104.3(2)	P(1)–C(11)–C(16)	122.1(5)
N–P(2)–C(41)	105.6(2)	P(1)–C(21)–C(22)	115.6(5)
C(31)–P(2)–C(41)	101.7(3)	P(1)–C(21)–C(26)	126.0(5)
P(1)–N–P(2)	122.8(3)	P(2)–C(31)–C(32)	121.9(5)
P(1)–N–C(1)	120.9(4)	P(2)–C(31)–C(36)	120.7(5)
P(2)–N–C(1)	116.1(4)	P(2)–C(41)–C(42)	126.0(5)
N–C(1)–C(2)	110.6(6)	P(2)–C(41)–C(46)	115.5(5)

(*c*) Torsion angles (°)

C(1)–N–P(1)–C(11)	−56.6(5)
C(1)–N–P(1)–C(21)	50.1(5)
C(1)–N–P(2)–C(31)	−129.8(4)
C(1)–N–P(2)–C(41)	123.4(4)
N–P(1)–C(11)–C(12)	−40.4(6)
C(21)–P(1)–C(11)–C(16)	41.0(6)
N–P(1)–C(21)–C(26)	−71.1(6)
C(11)–P(1)–C(21)–C(26)	36.4(6)
P(1)–N–C(1)–C(2)	−101.8(6)
P(1)–N–C(1)–C(3)	133.3(6)
P(2)–N–C(1)–C(2)	74.1(7)
P(2)–N–C(1)–C(3)	−50.8(7)
N–P(2)–C(31)–C(36)	47.0(6)
C(41)–P(2)–C(31)–C(32)	−33.4(6)
N–P(2)–C(41)–C(42)	60.3(7)
C(31)–P(2)–C(41)–C(42)	−48.4(7)

atoms P(1), P(2), N, and C(1) from their weighted least-squares plane is 0.025(4) Å], (*ii*) slight twisting of the PPh_2 groups about the P–N bonds, revealed by differences in magnitude of *ca.* 7° between C(isopropyl)–N–P–C(phenyl) torsion angles about the same P–N bond [C(1)–N–P(1)–C(11) and –C(21) −56.6(5) and 50.1(5)°, C(1)–N–P(2)–C(31) and –C(41) −129.8(4) and 123.4(4)°], and (*iii*) a twist of the isopropyl group about the N–C(1) bond of *ca.* 10° [P(2)–N–C(1)–C(2) and –C(3) respectively 74.1(7) and −50.8(7)°].

Bond lengths and angles within the phenyl and isopropyl groups are unexceptional. The conformations about the isopropyl C–C bonds are, as expected, close to staggered. The orientation of the phenyl groups with respect to the rest of the molecule does not accord even roughly with the C_s symmetry of the central skeleton, as may be seen from Figure 4. However, the two PPh_2 groups are conformationally similar. Thus the displacements of P(1), N, and C(21) from the mean plane through C(11)—C(16) are −0.30, 0.58, and 0.66 Å respectively; the corresponding values for P(2), N, and C(41) relative to the plane through C(31)—C(36) are −0.25, 0.79, and 0.55 Å. Contrastingly, the plane C(21)—C(26) passes within 0.02 Å of P(1), nearly bisecting N–P(1)–C(11), while C(41)—C(46) is within 0.01 Å of P(2), almost bisecting N–P(2)–C(31). These conformational differences are reflected in the P–C–C angles which are nearly equal at C(11) and C(31) whereas those at C(21) differ by 10°, as do those at C(41) (Table 3).

Structural data for this and other diphosphinoamines are summarised in Table 4. The P–N bond lengths in $Ph_2PN(Pr^i)PPh_2$ are equal to within experimental error. They agree well with corresponding values in diphosphinoamines of the C_{2v} conformeric type, provided the phosphorus substituents are amino or phenyl. Rather shorter P–N bond lengths are found in the halogenated species. In the C_{2v} conformers the angles at nitrogen appear to be sensitive to the steric size of the groups attached to nitrogen: the P–N–P angles are thus compressed to 115—117°, presumably to relieve R · · · X overcrowding, except when R = H. In $Ph_2PN(Pr^i)$-PPh_2, despite the bulk of the isopropyl group, the P–N–P angle is rather more open [122.8(3)°] and as a consequence the P · · · P separation is some 0.1 Å greater than in the C_{2v} conformers.

Although the foregoing data are generally consistent with the idea that increasingly bulky R substituents in diphosphinoamines result in an increase in the proportion of C_s conformers, there are two results that question the validity of this idea and also that of relating solution structures to those in the solid state. First, (1a) has a rather small *PNP* coupling (154 Hz) [4] and yet

TABLE 4

Structural data [a] for diphosphinoamines

Compound	Conformer [b]	P–N–P (°)	P–N(Å)	P · · · P(Å)	Ref.
(1a)	C_{2v}	120.7(4)	1.667(10)	2.898(3)	12
(1a)	C_{2v} [c,d]	122.1(7)	1.684(8)	2.948(14)	11
(1b)	C_{2v} [c]	116.1(8)	1.680(6)	2.851(10)	10
(3b)	C_{2v} [e]	117.4(3)	1.661(10)	2.838(10)	*f*
(R = Ph, X = NHPh)		117.8(3)			*g*
(5) [R = Ph, X_2 = $(NPh)_2PNHPh$]	Close to C_{2v}	115.4(4)	1.718(7) 1.702(7)	2.894	13
$[Ph_2PN(Me)PNBu^t]_2$	C_{2v} [h]	116.2(6)	1.728(12) 1.691(11)	2.903(5)	14
(2d)	C_s	122.8(3)	1.706(4) 1.711(4)	3.001(2)	This work

[a] Obtained by *X*-ray diffraction, except where otherwise noted. [b] Refers to local symmetry of the PNP skeleton only; small deviations from ideal symmetry are present in some cases. [c] Electron diffraction study. [d] Two conformers, one (72%) with PF_2 groups twisted by 5° from the C_{2v} form, and the second having one PF_2 group twisted by 58° from the C_{2v} form. [e] N.m.r. liquid crystal study, C_{2v} symmetry assumed. [f] I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Faraday Trans. 2*, 1977, 722. [g] A. D. Norman, R. C. Haltiwanger, and A. Tarassoli, Abstract INOR 260, 178th American Chemical Society Meeting, Washington D.C., 1979. [h] Analogous to C_{2v}.

has a solid-state C_{2v} conformation.[12] However a recent electron diffraction study [11] shows that only 72% of this compound adopts a conformation close to C_{2v} at ambient temperatures (Table 3). Our results also show that (2a) has a similar *PNP* coupling (158 Hz) at *ca.* 0 °C, which increases as the temperature is reduced. At -130 °C, the lowest temperature for which $^{31}P-\{^1H\}$ n.m.r. data were available, the spectrum broadened asymmetrically suggesting the presence of a mixture of conformers or tautomers (*cf.* ref. 19). These results are unexpected in terms of the steric effects of the hydrogen atom. Whilst the conformations of the fluoride will be influenced by $H \cdots F$ interactions in solution,[4] the NH-bridged diphosphinoamines in general merit further investigations.

Second, the *exo PNP* coupling of 3.0 Hz reported for (5) is totally out of line with its solid-state conformation which appears from a figure to be close to C_{2v}.[13] We have re-prepared this compound and its $^{31}P-\{^1H\}$ spectrum is in good agreement with that reported. Sharper signals can be obtained at lower temperatures where ^{14}N and/or exchange broadening effects are reduced. However, when the AA'BB' spectrum, which consists of two ' triplets,' was simulated it was found that its appearance is unchanged when any value of $J(PNP)(exo) \geqslant 3$ Hz is used [except for $J(PNP)$ $(exo) \sim \Delta\nu(A-B)$]. Therefore a large coupling that would be expected for the C_{2v} type of conformation fits the spectrum as well as the small value reported previously.[13]

It may be noted that $J(PNP)$ for the C_{2v} conformers increases in the order $[Ph_2PN(Me)PNBu^t]_2$ < (1b) < (3b) (estimated 660 Hz) [6] and that the $P \cdots P$ distances (Table 4) decrease in the same order. For C_{2v} conformers these results provide support for the notion [7,8] that $J(PNP)$ is related to the proximity of phosphorus lone pairs, but clearly such a correlation requires further justification given the uncertainties in $P \cdots P$ distances in solution.

EXPERIMENTAL

Hydrogen-1, ^{13}C, ^{19}F, and ^{31}P n.m.r. data were obtained as previously described.[5,18] The diphosphinoamines, (1b),[20] (3b, c, e) (R = Me, Et,[20] or Bu^t; [21] X = Cl), (2b, c, d) (R = Me,[22] Et,[22] or Pr^i; [5] X = Ph), and (4b, c) (R = Me or Et; X = NMe_2) [23] were prepared by literature methods.

Bis(difluorophosphino)-t-butylamine (1e).—Bis(dichlorophosphino)-t-butylamine, (3e) (2.4 g, 8.7 mmol), was mixed with antimony trifluoride (2.2 g, 12.3 mmol) in refluxing pentane (10 cm³) over a period of 3 h. Removal of the dark coloured solid and careful fractional distillation gave the *compound* (0.8 g, 48%) b.p. 82—85 °C [Found: C, 23.6; H, 4.4%; *m/e* 209. $C_4H_9F_4NP_2$ requires C, 23.0; H, 4.3%; *m/e* 209. ^1H N.m.r.: $\delta(CH_3)$ 1.53, $J(FPNCCH) = 0.7$ Hz].

Bis(dichlorophosphino)neopentylamine (3g).—A mixture of neopentylamine (2.2 g, 25 mmol) and triethylamine (5.05 g, 50 mmol) was added to phosphorus(III) chloride (6.9 g, 5.0 mmol) in diethyl ether (100 cm³) solution at -78 °C. The precipitate of triethylamine hydrochloride, and the diethyl ether, were removed leaving a pale yellow oil. Distillation under reduced pressure gave the *compound* (3.5 g, *ca.* 48%) b.p. 60—70 °C (0.1 mmHg) [Found: *m/e* 287. $C_5H_{11}Cl_4NP_2$ requires *m/e* 287 (for ^{35}Cl species)]. Phosphorus-31 n.m.r. spectroscopy showed that impurities amounting to *ca.* 10% were present including $(ClPNCH_2Bu^t)_2$, $\delta(P) + 241.3$. Hydrogen-1 and ^{31}P n.m.r. data were consistent with the above formulation.

Attempts to obtain bis(diphenylphosphino)-t-butylamine by a route similar to that used for the *N*-isopropyl analogue,[5] and by reaction of the *N*-lithio-derivative of diphenylphosphino-t-butylamine with chlorodiphenylphosphine in refluxing benzene solution, resulted in the formation of oily products, the major component in each case being tetraphenyldiphosphine oxide, $Ph_2P_AP_B(O)Ph_2$, identified by ^{31}P n.m.r. [δ_A, 35.9, δ_B -22.2, $J(PP) = 227.6$ Hz]. Identical ^{31}P n.m.r. parameters were obtained from an authentic sample.[24]

X-*Ray Analysis of* $Ph_2PN(Pr^i)PPh_2$ (2d).—*Crystal data.* $C_{27}H_{27}NP_2$, $M = 427.5$, Monoclinic, $a = 9.306(2)$, $b = 25.988(5)$, $c = 9.995(3)$ Å, $\beta = 98.76(2)°$, $U = 2\,389$ Å³, $Z = 4$, $D_c = 1.188$ g cm⁻³, $F(000) = 904$, space group $P2_1/n$ (C^5_{2h}, no. 14), equivalent positions $\pm(x, y, z)$; $\pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 1.6 cm⁻¹.

Measurements. The unit-cell dimensions and the integrated intensities of all independent reflections in the range $2 \leqslant \theta$ (Mo-K_α) $\leqslant 26°$ were measured using an Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator. Correction for background and Lorentz-polarisation effects yielded 1 269 reflections with $I \geqslant 3\sigma(I)$.

Structure analysis. The structure was solved by direct methods and refined by the full-matrix least-squares technique. In the final calculations the positions of all atoms were refined. Isotropic thermal parameters were adjusted for hydrogen atoms and anisotropic thermal parameters for other atoms. The refinement converged at *R*

TABLE 5

Fractional co-ordinates of non-hydrogen atoms (× 10^4) for (2d) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	2 684(2)	1 596(1)	2 902(2)
P(2)	4 008(2)	602(1)	4 012(2)
N	2 542(4)	965(2)	3 336(4)
C(1)	1 076(7)	706(3)	3 228(7)
C(2)	604(11)	664(4)	4 608(11)
C(3)	1 046(12)	186(4)	2 544(13)
C(11)	1 758(5)	1 614(3)	1 148(6)
C(12)	1 968(7)	1 214(3)	281(8)
C(13)	1 471(10)	1 260(4)	−1 092(9)
C(14)	809(8)	1 692(4)	−1 611(8)
C(15)	580(8)	2 080(3)	−809(9)
C(16)	1 060(8)	2 051(3)	587(8)
C(21)	1 404(7)	1 956(2)	3 796(6)
C(22)	2 025(8)	2 254(2)	4 842(7)
C(23)	1 185(11)	2 544(3)	5 604(8)
C(24)	−283(12)	2 520(3)	5 301(9)
C(25)	−908(8)	2 225(3)	4 289(10)
C(26)	−89(8)	1 942(3)	3 501(7)
C(31)	5 001(7)	1 011(2)	5 313(6)
C(32)	6 500(8)	1 019(3)	5 564(8)
C(33)	7 221(10)	1 260(4)	6 668(10)
C(34)	6 530(12)	1 521(4)	7 528(9)
C(35)	5 052(12)	1 521(3)	7 325(8)
C(36)	4 284(8)	1 268(3)	6 226(7)
C(41)	5 234(6)	597(3)	2 722(5)
C(42)	5 856(8)	1 018(3)	2 229(8)
C(43)	6 739(8)	969(4)	1 257(8)
C(44)	7 029(10)	502(5)	792(10)
C(45)	6 441(15)	93(4)	1 263(12)
C(46)	5 528(10)	126(3)	2 244(8)

0.035, R' 0.042. The final-difference synthesis ($|\Delta_\rho| < 0.35$ e Å^{-3}) and weighting analysis were satisfactory. Anomalous dispersion corrections and neutral-atom scattering factors were taken from ref. 25. Programs used were SHELX (G. M. Sheldrick), CAD4 (M. B. Hursthouse), ORTEP (C. K. Johnson), and GEOM (P. R. Mallinson).

Final co-ordinates for non-hydrogen atoms are given in Table 5. Supplementary Publication No. SUP 23102 (11 pp.)* contains hydrogen-atom positions, anisotropic thermal parameters, and observed and calculated structure amplitudes.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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