Phosphorus–Nitrogen–*Phosphorus* Spin Coupling in the Nuclear Magnetic Resonance Spectra of some Cyclodiphosph(III)azanes

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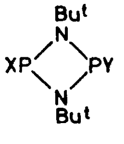
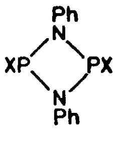
The magnitude and sign of the coupling constant $^2J(PNP)$ has been obtained from the n.m.r. spectra of a series of cyclodiphosphazanes, $\overline{XPNBu^tP(Y)NBu^t}$ (X = Y = F, Me, OMe, or NMe_2; X = Cl, Y = F, OMe, or NMe_2; X = F, Y = NMe_2), $\overline{XPNPhP(X)NPh}$ (X = OMe or NMe_2), and $\overline{Bu^tNP(NMe_2)NBu^tP}^+AlCl_4^-$ by single- and double-resonance methods. More positive *PNP* couplings are found in those derivatives where X and Y are of relatively high electron-withdrawing power, although chlorine-containing compounds have more positive couplings than analogous fluorine-containing compounds. When X = Y = OMe or NMe_2, geometrical isomers have *PNP* couplings of opposite sign.

THE coupling constant $J(PNP)$, involving two tervalent phosphorus atoms, covers a wide range (*ca.* −35 to 446 Hz) and its magnitude is related to the conformation adopted by the P–N bonds in solution.[1] This coupling constant may also be related to the electron-supplying power of the phosphorus and nitrogen substituents, but in a manner which is difficult to distinguish from conformational effects. The recent isolation [2-5] of several cyclodiphosphazanes of types (1) and (2) provides an opportunity to examine the effects of the substituents X and Y on $^2J(PNP)$ without large changes in the mutual conformations of the two phosphorus atoms. In four cases, (1; X = Y = NMe_2 or OMe) and (2; X = NMe_2 or OMe), geometrical isomers were available, and the signs of their *PNP* couplings have been compared.


(1)


(2)

RESULTS

A re-examination of the ^{19}F n.m.r. spectra of the 2,4-difluoro-derivative (1; X = Y = F) [6] resulted in a similar set of parameters to those originally obtained,[6] except that ^{19}F-$\{^{31}P\}$ double-resonance experiments have now been used to establish the signs of $J(PNP)$ [$= {^2J}(PP')$] and $^4J(FF')$ relative to $^1J(PF)$ and to $^3J(PF')$. The energy-level diagram for this $AA'XX'$ spin system [neglecting a coupling $^4J(PNCCH)$ of 0.7 Hz] shows [7] that each component of the intense ' *N* doublet ' in the ^{19}F spectrum is connected with the *N* doublet (transitions 1—2 and 3—4) and two of the transitions (5—7 or 6—8) in the ^{31}P spectrum. The connection between the ^{19}F and ^{31}P spectra obtained by monitoring the *N* doublet in the ^{19}F spectrum and irradiating

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[2] G. Bulloch and R. Keat, *J.C.S. Dalton*, **1976**, 1113.

[3] G. Bulloch, R. Keat, and D. G. Thompson, *J.C.S. Dalton*, **1977**, 99.

[4] O. J. Scherer and G. Schnabl, *Chem. Ber.*, 1976, **109**, 2296.

[5] W. Zeiss and J. Weis, *Z. Naturforsch.*, 1977, **B32**, 485.

[6] J. F. Nixon and B. Wilkins, *Z. Naturforsch.*, 1970, **B25**, 649.

[7] See, for example, R. J. Abraham, ' Analysis of High Resolution N.M.R. Spectra,' Elsevier, Amsterdam, 1971, p. 310. The numbering of transitions is taken from this reference also.

the ^{31}P spectrum is shown in Figure 1. This distinguishes $^2J(PP') + {}^4J(FF')$ and $^2J(PP') - {}^4J(FF')$, and gives the relative signs of $^2J(PP') + {}^4J(FF')$ and $^1J(PF) + {}^3J(PF')$ ($=N$). $^2J(PP')$ and $^4J(FF')$ are opposite in sign to $^1J(PF)$, but the former two couplings are not distinguished (see below).

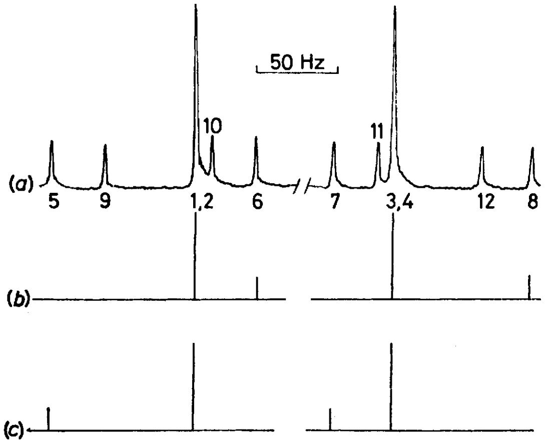

FIGURE 1 (*a*) Fluorine-19 n.m.r. spectrum of (1; X = Y = F); (*b*) ^{31}P transitions detected by monitoring transition 1—2 in (*a*) (diagrammatic); (*c*) as in (*b*), but monitoring transitions 3—4

$^2J(PP')$ was measured directly from the ^1H spectra of the isomeric methoxy-derivatives (1; X = Y = OMe) and the methyl derivative (1; X = Y = Me),[4] using the relations previously established for the $X_3AA'X_3'$ spin system[8] (again ignoring the small couplings to the Bu^t protons). The relative sign of $^2J(PP')$ was obtained by $^1H-\{^{31}P\}$ INDOR experiments. These take advantage of the connection between the components of the *N* doublet in the ^1H spectrum and a multiplet in the ^{31}P spectrum which is separated from the main ^{31}P signal by (approximately) $^2J(PP')$. The position of the outer multiplet relative to the main ^{31}P signal determines the sign of $^2J(PP')$ relative to $J(PZCH) + J(PNPZCH)$ (Z = oxygen or nothing).[9,10] For example, the $^1H-\{^{31}P\}$ INDOR spectra of (1; X = Y = OMe) (Figure 2), which are devoid of fine structure, show that the high-frequency component of the *N* doublet is connected with the high-frequency group of outer lines in the ^{31}P spectrum. $^2J(PP')$ and $^3J(PH) + {}^5J(PH')$ are therefore of the same sign; since $^5J(PH')$ is small and $^3J(PH)$ is known to be positive in methoxyphosphines,[11] then $^2J(PP')$ is positive. For reasons which are not clear, there was insufficient detail resolved in the ^1H spectra of the isomeric forms of (1; X = Y = NMe_2) to obtain $^2J(PP')$ accurately, so that rough estimates of this parameter could only be made from the INDOR spectra. In ref. 10, where $^1H-\{^{31}P\}$ INDOR spectra of transition-metal complexes were examined, the separation between outer groups of lines was found to be $|J(PP')| + |[9L^2 + J(PP')^2]^{\frac{1}{2}}|$ [$L = {}^3J(PH) - {}^5J(PH')$] which corresponded to the $\alpha\alpha(m,p)$, $\beta\beta(m,p)$ states of the ^{31}P nuclei, where m and $p = +\frac{3}{2}$ and $-\frac{3}{2}$ respectively. In cases where $^2J(PP')$ could be measured accurately from the ^1H spectra of cyclodiphosphazanes, the separation of the outer lines in the $^1H-\{^{31}P\}$ INDOR spectra was no more than $|J(PP')| + |[L^2 + J(PP')^2]^{\frac{1}{2}}|$, which corresponds to the states where m and p are $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively. The isomer of (1; X = Y = NMe_2) giving the low-field ^{31}P shift has two *N*-methyl signals at room temperature because of restricted rotation about the exocyclic P–N bond.[12] It was only possible to measure the INDOR spectra from one component of the *N* doublet [$^3J(PH) + {}^5J(PH')$ 12.2 Hz] (because of overlap with the other *N* doublet) suggesting that $^2J(PP')$ is negative. However, ^{31}P coupling to the Bu^t protons was easily resolved [$^4J(PNCCH)$ 0.8 Hz] and $^1H-\{^{31}P\}$ INDOR showed that $^2J(PP')$ and $^4J(PNCCH)$ had opposite signs (following the reasoning in ref. 13). There is good reason to believe that the latter coupling is positive (see below). The relative signs of $^2J(PP')$ and $^3J(PZCH) + {}^5J(PNPZCH)$ (*Z* = O or N) in the two isomeric forms of (2; X = OMe) and of (2; X = NMe_2) were measured by the INDOR technique.

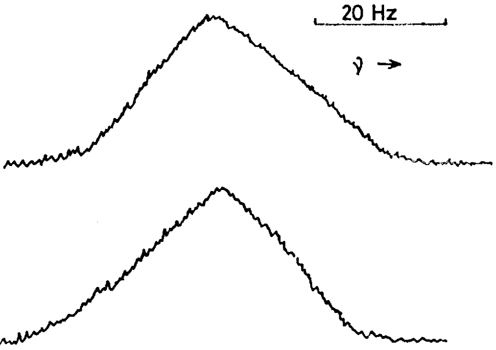

FIGURE 2 (*a*) $^1H-\{^{31}P\}$ INDOR spectrum of (1; X = Y = OMe), δ_P 133.7 p.p.m., monitoring the high-frequency component of the *N* doublet in the ^1H spectrum; (*b*) as in (*a*) but monitoring the low-frequency component of the *N* doublet. The 'outer' multiplets are not resolved, but their positions are revealed by the asymmetry of the spectra

The n.m.r. parameters for compounds (1; X ≠ Y) were obtained by direct observation and by $^1H-\{^{31}P\}$ and/or $^{19}F-\{^{31}P\}$ double-resonance experiments. For (1; X = Cl, Y = F) and (1; X = F, Y = NMe_2), $^1J(PF)$ (known to be negative[14]) was of opposite sign to $^2J(PP')$. Compound (1; X = Cl, Y = OMe) had a five-bond $P \cdots H$ coupling to the methoxy-protons of 0.3 Hz, so that the relative signs of $^3J(POCH)$ and $^2J(PP')$ could be compared. These were of the same sign and $^3J(POCH)$ is assumed to be positive.[11] The two four-bond couplings to the Bu^t protons in this compound were positive and it is assumed that this is the case in determining the sign of $J(PP')$ in (1; X = Cl, Y = NMe_2) and in $Bu^t\overline{NP(NMe_2)NBu^tP}^+AlCl_4^-$.

DISCUSSION

Of the symmetrical cyclodiphosphazanes, the difluoro-compound, (1; X = Y = F), has the most positive $J(PP')$, but the 92.5 Hz, originally assigned[6] to this

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[8] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

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[14] R. R. Dean and W. McFarlane, *Chem. Comm.*, 1967, 840; A. V. Cunliffe, E. G. Finer, R. K. Harris, and W. McFarlane, *Mol. Phys.*, 1967, **12**, 497.

TABLE 1

Hydrogen-1 and ^{31}P n.m.r. data for cyclodiphosphazanes (1) and (2) [a]

X	Y	$^2J(PP')$/Hz	δ_P/p.p.m.	$^3J(PZCH)$ [b]/Hz	$\delta(PZCH)$/p.p.m.	$^4J(PNCCH)$/Hz	$\delta(PNCCH)$/p.p.m.
Compound (1)							
F	F	+30.7 ±1 [c]	165.6			0.7	1.35
OMe	OMe	+15.9 ±0.5	133.7	+10.1	3.48	⩽0.3	1.29
OMe	OMe	−9.5 ±0.5	202.4	+9.0	3.65	+0.7	1.24
NMe_2	NMe_2	+14 ±5	95.0	+8.0	2.66	<0.3	1.17
NMe_2	NMe_2	−10 ±5	184.7	+3.2 [d] +12.2	2.63 2.74	+0.8	1.13
Me	Me	+8.5 [e]	170.6	+6.4(PCH_3)	1.61	0.5	1.03
Cl	F	+49.6 ±0.5	197.1(*P*Cl) 180.3			+0.9 *ca.* +0.9	1.40
Cl	OMe	+39.2 ±0.5	188.7(*P*Cl) 139.4	+8.1 [f]	3.75	+0.8(*P*Cl) +0.6	1.38
Cl	NMe_2	+32.5 ±0.5	186.6(*P*Cl) 131.5	+12.6 [d] +4.1	2.80 2.80	+0.7(*P*Cl) +0.5	1.29
Cl	Me	33.0 [g]	237.0(*P*Cl) [g] 200.4				
F	NMe_2	+14.0 ±0.5	145.9(*P*F) 116.3	+13.7 [d,h] +2.8	2.70 [h] 2.55	0.3(*P*F) 0.5	1.24
$Bu^tNP(NMe_2)NBu^tP^+AlCl_4^-$		+58 ±5	124.3($PNMe_2$) 331.5	+15.1 [d,i] +3.7	2.84 [i] 2.46	+1.2(P^+) +0.7	1.43
Compound (2)							
OMe	OMe	>0 [j]	137.2	+10.2	3.50		
OMe	OMe	<0 [j](11.75) [k]	187.5	+9.3	3.31		
NMe_2	NMe_2	>0 [j]	101.0	+8.7	2.87		
NMe_2	NMe_2	<0 [j]	166.5	+8.4	2.78		

[a] For $CDCl_3$ solutions at *ca.* 33 °C, except where otherwise stated. Phosphorus-31 shifts are downfield (positive) from 85% H_3PO_4 (external). All the compounds, except (1; X = Cl, Y = F) and (2), were examined as pure single isomers. [b] When $X \neq Y$; however, when X = Y, this term is $^3J(PZCH_3) + {}^5J(PNPZCH_3)$. [c] Ref. 6 gives 92.5 Hz. [d] Two *N*-methyl signals because of restricted rotation about the exocyclic P–N bond. [e] Ref. 4; all data from solution in C_6H_6. [f] $^5J(PNPOCH) = -0.3$ Hz. [g] Data from ref. 4; solution in CD_3CN. [h] Chlorobenzene solution at −15 °C. [i] *o*-Dichlorobenzene solution. [j] Benzene solution; $^2|J(PP')| < 30$ Hz. Overlap of signals from the two isomers precludes definite measurement of $J(PP')$. [k] From ref. 5; the ^{31}P shifts given in this reference suggest that shifts of the order of 5 p.p.m. occur on changing from $CDCl_3$ to C_6H_6 solution.

TABLE 2

Fluorine-19 n.m.r. data for compounds (1) [a]

X	Y	δ_F [b]/p.p.m.	$^1J(PF)$/Hz	$^3J(PF')$/Hz	$^4J(FF')$/Hz
F	NMe_2	−17.8	−1 149 ± 1	−14.9 ± 0.5	
F	F	−21.9	−1 181 ± 1	+22.5 ± 1	+94.8 ± 1
F	Cl	−26.5	−1 189 ± 1	+59.0 ± 1	

[a] Samples in $CDCl_3$ solution at *ca.* 33 °C. [b] Upfield (negative) relative to CCl_3F (external).

compound is something of an enigma, since $^2J(PP')$ and $^4J(FF')$ cannot be distinguished. If changes in $^2J(PP')$ are dominated by electronegativity effects, then 30.7 Hz represents the best progression from the other compounds where X = Y. The result obtained for (1; X = Cl, Y = F) might at first sight favour the assignment of a larger coupling to the difluoride, but a comparison with (1; X = F, Y = NMe_2) shows that a chlorine, rather than a fluorine, substituent gives the larger P···P coupling. Further, the ^{19}F n.m.r. data (Table 2) for (1; X = F; Y = NMe_2, F, or Cl) show that there is a close parallel between $^3J(PF')$ and $^2J(PP')$, but only when $^2J(PP')$ is 30.7 Hz for (1; X = Y = F). This assumes that the compounds in Table 2 all have the same (*cis*) structure; unambiguous evidence for this is lacking. The foregoing assignment to $^2J(PP')$ leaves an exceptionally large value for $^4J(FF')$ of 94.2 Hz, which may be compared with the same parameter in diphosphinoamines, $F_2P{\cdot}NR{\cdot}PF_2$ (R = H,[15] alkyl,[16,17] or aryl[16]), where it is <11.7 Hz. In view of the fact that through-space F···F couplings are likely to be positive, it is tempting to suggest that $^4J(FF')$ has a sizeable through-space contribution and that (1; X = Y = F) must have a 2,4-*cis* arrangement of fluorine atoms. No structural information has been reported for this molecule, but the analogous chloride, (1; X = Y = Cl), has a *cis* structure.[18] The view has been expressed that at distances of >2.5 Å, F···F through-space coupling effects will be small.[19] The Cl···Cl non-bonded distance in (1; X = Y = Cl) is 4.10 Å,[18] and this distance is hardly likely to be <3 Å in the di-

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[15] D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975, 889.

[16] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087.

[17] R. W. Rudolf and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

[18] K. W. Muir, *J.C.S. Dalton*, 1975, 259.

[19] A. D. Buckingham and J. E. Cordle, *J.C.S. Faraday II*, 1974, 994.

fluoride unless the cyclodiphosphazane ring is appreciably more distorted from planarity than in the dichloride.

It is an interesting finding that the geometrical isomers of the bismethoxy- and bis(dimethylamino)-derivatives have P · · · P couplings of opposite sign. Those isomers of (1) with the highest-field ^{31}P shift have been assigned *cis* structures.[20] These findings appear to be in contrast with the results obtained [21] for *cis* and *trans* isomers of $(Bu^tPNMe)_2$, where the couplings $^2J(PP')$ are 28.0 and 24.3 Hz respectively, unless these are of opposite sign. Only two crystal structures of compounds containing the cyclodiphosph(III)azane ring system have been reported,* and these show that the ring is slightly puckered in *cis*-(1; X = Y = Cl),[18] but planar in *trans*-$[(Me_3Si)_2NPNSiMe_3]_2$.[22]

When cyclodiphosphazanes (1; X = Y) of probable *cis* structure are compared increasingly positive $^2J(PP')$ values are found in the series: X = Y = NMe_2, X = Y = OMe, and X = Y = F. In view of the results for the non-symmetrical compounds (X ≠ Y), it appears that the most positive $^2J(PP')$ coupling would apply to (1; X = Y = Cl). There is a similar trend to more positive P · · · P′ couplings for compounds (1; X ≠ Y), although the value [4] of 33.0 Hz for (1; X = Cl, Y = Me) is somewhat larger than anticipated (if positive). A related general trend in *PNP* couplings has been noted for cyclic [23,24] and acyclic [25,26] phosphorus(V) compounds, although in these cases it was the fluorine-, rather than chlorine-, substituted derivatives that had larger positive P · · · P couplings.

The reduced conformational mobility of the ring systems (1) and (2), relative to the acyclic diphosphinoamines,[1] is reflected in the much smaller range of P · · · P couplings. If conformational effects were important in determining these relatively small variations in $^2J(PP')$ for isomers of like structure it might be anticipated that increasing electronegativity of X (or Y) substituents would make this coupling less positive. This is because increasing electron withdrawal by X (or Y) will result in smaller XPN angles,[27] and a larger P–N–P–lone pair dihedral angle, which is expected to result in a less-positive P · · · P′ coupling.[1] An extreme case of this effect is to be found in the adduct $Bu^tN\overline{P(NMe_2)NBu^tP}^+$-$AlCl_4^-$. Here, where the $>P^+$ atom is effectively bonded to a substituent of high electronegativity, and the lone pair is bisected by the plane of the ring, $^2J(PP')$ is relatively large (58 Hz) and positive. $|^2J(PP')|$ is 36.0 Hz in $Bu^t\overline{NP(Me)NBu^tP}^+AlCl_4^-$.[4]

The reasons for the difference in sign of $^2J(PP')$ for the pairs of geometrical isomers are not readily apparent. Even though the dihedral angles relating the two phosphorus atoms may not change much between *cis* and *trans* isomers, there are considerable differences in non-bonded electron-pair interactions (as evidenced by photoelectron spectroscopy [28]) to be taken into account.

EXPERIMENTAL

Compounds (1; X = Y = F), b.p. 60—70° C (2 mmHg) {this result was carefully checked and the b.p. reported in ref. 6 [23.5 °C (4 mmHg)]† appears to be in error}, (1; X = Y = Me),[4] (1; X = Cl, Y = NMe_2),[3] and (2; X = Y = NMe_2 [3] or OMe [29]) were prepared by literature methods. The separation of isomeric forms of (1: X = Y = NMe_2; X = Y = OMe) will be described elsewhere,[30] as will the preparation of (1; X = Cl, Y = OMe).[30] A mixture containing (1: X = Cl, Y = F; X = Y = Cl; and X = Y = F) was obtained by heating the latter two compounds (1 : 1 molar proportions) together at *ca.* 100° C for 24 h. The proportions of the three compounds were *ca.* 2 : 1 : 1 respectively.

Compound (1; X = F, Y = NMe_2) was obtained by mild fluorination of (1; X = Cl, Y = NMe_2) as follows. Compound (1; X = Cl, Y = NMe_2) (2.97 g, 10.5 mmol) in pentane (20 cm^3) was stirred with anhydrous antimony trifluoride (3.46 g, 19.3 mmol) at ambient temperatures for 12 h. The dark coloured solid and the solvent were removed to leave a colourless oil. The oil was purified by distillation under reduced pressure to give *2-dimethylamino-4-fluoro*-1,3-*di-t-butylcyclodiphosphazane* (1.4 g, 50%), b.p. 62 °C (1.2 mmHg) (Found: C, 44.6; H, 9.0, N, 15.4_5%; *m/e* 267. $C_{10}H_{24}FN_3P_2$ requires C, 44.9; H, 9.0; N, 15.7%; *m/e* 267).

The adduct $Bu^t\overline{NP(NMe_2)NBu^tP}^+AlCl_4^-$ was prepared by addition of a slight excess of 1 mol equivalent of anhydrous aluminium chloride to (1; X = Cl, Y = NMe_2) in methylene chloride solution. A pure sample was not obtained, but the formulation is consistent with the integrated ^1H spectrum and with the published [4] ^1H and ^{31}P n.m.r. data for the analogous methyl compound $Bu^t\overline{NP(Me)NBu^tP}^+AlCl_4^-$.

Hydrogen-1 and ^{19}F n.m.r. spectra were obtained on a JEOL C60HL spectrometer at *ca.* 60 and 56.4 MHz respectively. Double-resonance experiments were carried out on the same spectrometer as previously described.[1] ^{19}F-$\{^{31}P\}$ double-resonance experiments were carried out with the spectrometer operating in the 'field-sweep' mode, but the intepretation of the results was simplified by altering the

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* The crystal-structure determination of the isomer of (2; X = OMe) having δ_P 137.2 p.p.m. shows that this has a *trans* structure (W. Schwarz, H. Hess, and W. Zeiss, unpublished work).

† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[20] R. Keat, A. N. Keith, A. MacPhee, K. W. Muir, and D. G. Thompson, *J.C.S. Chem. Comm.*, in the press.

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[27] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand–Reinhold, London, 1972.

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[29] T. Kawashima and N. Inamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 1924.

[30] R. Keat, D. S. Rycroft, and D. G. Thompson, unpublished work.

^{19}F observation frequency so that all $\{^{31}P\}$-irradiation experiments were made at constant field. Final parameters for the ^{31}P spectra of the fluorine-containing compounds were obtained from a Varian XL-100 spectrometer at *ca.* 40.5 MHz.

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