Nuclear Magnetic Resonance Studies of Rotation about Phosphorus–Nitrogen Bonds in Dialkylaminocyclodiphosphazanes†

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The ^{1}H n.m.r. spectra of dimethylaminocyclodiphosphazanes, X[P·NR^1·PY·NR^2] [X = Cl, Y = NMe_2, R^1 = Me, R^2 = Bu^t, R^1 = R^2 = Bu^t, R^1 = R^2 = Ph; X = Y = NMe_2, R^1 = Me, R^2 = Bu^t, R^1 = R^2 = Bu^t, R^1 = R^2 = C_6H_4Z-*p* (Z = H, Cl, Me, and OMe)], at, or below, ambient temperatures show that in some cases the dimethylamino-protons are non-equivalent. Measurements of the free energy of activation ($\Delta G^{\ddagger}_{T_c}$) in these, in the diethylamino-derivatives, (Et_2N)[P·NR·P(NEt_2)·NR] (R = Bu^t and Ph), and in the di-isopropylamino-derivative, Cl[P·NBu^t·P(NPr^i_2)·NBu^t], indicate that the non-equivalence is due to restricted rotation about the exocyclic phosphorus–nitrogen bonds. Exceptionally high barriers are found for one of the two possible isomeric forms of Cl[P·NBu^t·P(NMe_2)·NBu^t] and of (Me_2N)[P·NBu^t·P(NMe_2)·NBu^t] (16.9 and 17.6 kcal mol^{-1} respectively), and there are substantial differences in $\Delta G^{\ddagger}_{T_c}$ (3–6 kcal mol^{-1}) for pairs of geometrical isomers. The ^{31}P chemical shifts of the aminocyclodiphosphazanes, measured by ^{1}H-{^{31}P} double resonance, are temperature dependent, and this dependence is discussed in relation to possible conformational effects.

It is well established that variable-temperature ^{1}H n.m.r. spectroscopy can be used to detect restricted rotation about certain tervalent phosphorus–nitrogen bonds.[1] For example in $PPhCl(NMe_2)$, the aminophosphine most extensively investigated, the free energy of activation, $\Delta G^{\ddagger}_{T_c}$, for rotation about the P–N bond is 10.9 kcal mol^{-1} at −50 °C (T_c).[1,‡] Attempts to identify the factors contributing to the barrier have had mixed success. There is a clear steric dependence on the nitrogen substituents as illustrated by the decrease in $\Delta G^{\ddagger}_{T_c}$ from 17.5 to 8.4 kcal mol^{-1} for $PCl_2(NBu^t_2)$ [2] and $PCl_2(NMe_2)$ [1] respectively, and by the lower barriers to P–N bond rotation observed in $PRCl(NMe_2)$ relative to $PRCl(NPr^i_2)$ (R = Me [3,4] or Ph [1,4]). The barrier ($\Delta G^{\ddagger}_{T_c}$) increases slightly (0.4 kcal mol^{-1}) with increasing size of the phosphorus substituent in $PRCl(NPr^i_2)$ (R = Me or Bu^t),[4] but unexpectedly *decreases* with increasing size of the phosphorus substituent in the series $PRCl(NMe_2)$ (R = Me, Ph, or Bu^t).[3,4]

The results of photoelectron (p.e.) spectroscopy on the series of aminophosphines, $PCl_{2-n}(CF_3)_n(NMe_2)$ (n = 0,

† No reprints available.

‡ Throughout this paper: 1 cal = 4.184 J.

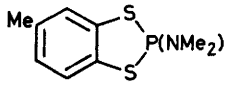
[1] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206.

[2] O. J. Scherer and N. Kuhn, *Chem. Ber.*, 1975, **108**, 2478.

[3] S. DiStephano, H. Goldwhite, and E. Mazzola, *Org. Magnetic Resonance*, 1974, **6**, 1.

[4] J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J.C.S. Perkin II*, 1976, 1052.

1, or 2), have been interpreted to indicate that the barrier arises from lone-pair–lone-pair repulsion effects and from steric effects,[5] rather than from $(p–d)\pi$ bonding. The interpretation of the p.e. spectra has, however, since been disputed by other workers.[6] A common feature of almost all the aminophosphines in which P–N rotational barriers have been measurable[7] by n.m.r. is that phosphorus is bonded to a halogen atom or an alkoxy-group. However, the incorporation of phosphorus into a five-membered ring, for example as in (A), has been shown[8] to result in an increase in the

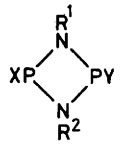


(A)

barrier to P–N rotation relative to the acyclic compound, $P(NMe_2)(SEt)_2$. Very recently a crystal-structure study[9] of $[(Me_3Si)N{\cdot}P{\cdot}N(SiMe_3)_2]_2$ has established that the bis(trimethylsilyl)amino-groups have a mutual *trans* orientation with respect to the cyclodiphosphazane ring, and n.m.r. data for the same compound indicate that the exocyclic P–N bond has a very high barrier to rotation ($\Delta G^{\ddagger}_{T_c} > 27$ kcal mol^{-1}).

RESULTS

Our results show that certain dimethylaminocyclodiphosphazanes (1; X = Y = NMe_2) exhibit coalescence phenomena at considerably higher temperatures than acyclic dimethylaminophosphines. Interest in this topic arose from observations[10] on the monodimethylamino-derivative (1; X = Cl, Y = NMe_2, $R^1 = R^2 = Bu^t$) and the bis(dimethylamino)-derivative (1; X = Y = NMe_2, $R^1 = R^2 = Bu^t$) at, or near, ambient temperatures. The

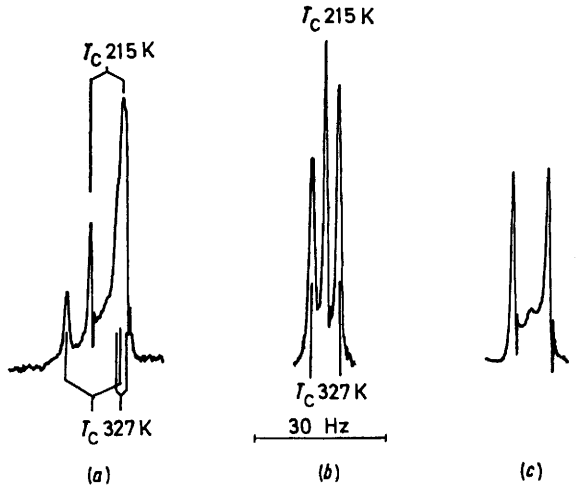


(1)

^{1}H n.m.r. spectra of these two derivatives showed more dimethylamino-proton signals than might be expected. For example, the bis(dimethylamino)-derivative showed three dimethylamino-proton signals (after ^{31}P decoupling), although only two geometrical isomers were known to be present (Figure). On heating, two of the signals coalesced at 327 K, and on cooling four dimethylamino-proton signals were observed. The free energies of activation for the two rate processes were estimated as 17.6 and 11.4 kcal mol^{-1}. The former value is exceptionally high to be assigned to the barrier to rotation about the P–N bond. We therefore examined the variable-temperature spectra of other cyclodiphosphazanes to ascertain the origin of the rate process.

Dimethylaminocyclodiphosphazanes (1; X = Y = NMe_2, $R^1 = Bu^t$, R^2 = Me, Et, or Bu^t) are formed as a mixture of geometrical isomers,[10] with large ^{31}P chemical-shift differences between the isomers (up to 90 p.p.m.). When R^1 and R^2 = alkyl the isomer with the ' high-field ' ^{31}P shift was the most thermodynamically stable form, but when $R^1 = R^2$ = aryl the isomer with the ' low-field ' shift was thermodynamically favoured. The data in Table 1 show the coalescence temperatures observed under conditions of complete ^{31}P decoupling, when the calculation of $\Delta G^{\ddagger}_{T_c}$, from observations on the collapse of two uncoupled singlets, using the relation $k = \pi\Delta\nu/2^{\frac{1}{2}}$, is valid.[11] In each case the isomer with the ' low-field ' ^{31}P shift has the highest free energy of activation for the rate process. For both isomeric forms, $\Delta G^{\ddagger}_{T_c}$ could only be compared for (1; X = Y = NMe_2; R^1 = Me, $R^2 = Bu^t$ and $R^1 = R^2 = Bu^t$), although an upper estimate could be made when coalescence phenomena were not observed.

Increasing size of the R^2 group in compounds (1; X = Y = NMe_2, $R^1 = Bu^t$, R^2 = Me or Bu^t) results in an increase in the barrier and indicates a steric dependence on the ring N substituent. A steric dependence on the size of



Hydrogen-1 n.m.r. spectra (60 MHz) in benzene solution at 280 K of (*a*) a mixture of isomers of $(Me_2N)\overline{P{\cdot}NBu^t{\cdot}P(NMe_2)}{\cdot}NBu^t$, distinguished by their coalescence temperatures (T_c), (*b*) as in (*a*) but with complete ^{31}P decoupling, and (*c*) the pure isomer (T_c 215 K) obtained after heating the mixture in (*a*)

the dialkylamino-group is indicated when (1; X = Y = NMe_2 or NEt_2, $R^1 = R^2$ = Ph) are compared ($\Delta G^{\ddagger}$ 12.6 and 13.8 kcal mol^{-1} respectively). The same effect is apparent for (1; X = Cl, Y = NMe_2 or NPr^i_2, $R^1 = R^2 = Bu^t$) ($\Delta G^{\ddagger}_{T_c}$ 16.9 and 19.5 kcal mol^{-1} respectively). The barriers for (1; X = Y = NMe_2 or NEt_2, $R^1 = R^2 = Bu^t$) appear to be similar in magnitude, although the methylene-proton signals of the diethylamino-compound broadened at *ca.* 220 K and did not sharpen up again, even at 180 K.

In general it was easier to measure $\Delta G^{\ddagger}_{T_c}$ for dimethylamino-groups when $R^1 = R^2$ = aryl, where the thermodynamically favoured isomer has the highest barrier, than

[5] A. H. Cowley, M. J. S. Dewar, J. W. Gilje, D. W. Goodman, and J. R. Schweiger, *J.C.S. Chem. Comm.*, 1974, 340.

[6] M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer, and E. Unger, *J.C.S. Dalton*, 1975, 1207.

[7] For a recent summary, see R. H. Neilson, R. Chung-Yi Lee, and A. H. Cowley, *J. Amer. Chem. Soc.*, 1975, **97**, 5302.

[8] H. Boudjebel, H. Gonçalves, and F. Mathis, *Bull. Soc. chim. France*, 1975, 628.

[9] E. Niecke, W. Flick, and S. Pohl, *Angew. Chem. Internat. Edn.*, 1976, **15**, 309.

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

[11] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

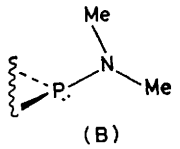
when $R^1 = R^2$ = alkyl. No activation parameters were determined for the isomers apparently formed as a result of kinetic control when $R^1 = R^2$ = aryl, because of the low concentrations of these forms. There were two notable results for the thermodynamically favoured isomers. First, the barriers are all equal within experimental error (12.5—12.7 kcal mol^{-1}) and, secondly, they are higher than those observed for the thermodynamically favoured isomer where $R^1 = R^2 = Bu^t$. If the thermodynamically favoured isomers have the same structure then steric effects would be expected to produce the opposite trend; this result may indicate that the thermodynamically favoured isomers have different geometric configurations.

The effect of replacing a dimethylamino-group by a chlorine atom to give (1; X = Cl, Y = NMe_2, $R^1 = R^2$ = alkyl or aryl) depends on the R^1 and R^2 substituents. Thus the barrier is significantly raised relative to that in the isomer with the 'low-field' ^{31}P shift when $R^1 = Bu^t$, R^2 = Me and when $R^1 = R^2$ = Ph, but not when $R^1 = R^2 = Bu^t$. The high barrier observed for (1; X = Cl, Y = NPr^i_2, $R^1 = R^2 = Bu^t$) is to be expected. In this case the shift between the methyl signals was 0.26 p.p.m., compared with a surprisingly large shift of 1.22 p.p.m. between the methine signals at ambient temperatures.

DISCUSSION

The observed steric effects, particularly those produced on increasing the size of the dialkylamino-groups, indicate that the barriers measured relate to rotation about the exocyclic P–N bonds, rather than to inversion at the exocyclic nitrogen atoms. The barriers are too low to be related to inversion at phosphorus.[12] We also discount the possibility that the coalescence phenomena might be related to the formation of monomeric phosphazenes, $R^1_2N{\cdot}P{=}N{\cdot}R^2$, or to the presence of trimeric cyclophosphazanes. For example, the monomer species would be expected to have a very low-field ^{31}P shift [9,13] and the latter species would not be expected to show large $^3J(PH)$ coupling constant differences (see below) relative to the dimers (1).[14]

The appearance of anisochronous *N*-methyl protons in those derivatives (1; $R^1 = R^2$) clearly demonstrates that the preferred conformation is one in which the methyl groups lie in, or close to, the plane passing through the two phosphorus atoms and perpendicular



(B)

to the cyclodiphosphazane ring (B). This conformation is that expected on the basis of numerous structural studies of tervalent phosphorus–nitrogen compounds [7] in which the lone pair of electrons on nitrogen (in an orbital with substantial *p* character) lies orthogonal to the lone pair on phosphorus. Molecular models suggest that this would also be the conformation in which steric interactions are minimised, particularly in the *trans* isomer. There is good evidence [1,14] that the methyl group *cis* to the lone pair on phosphorus will have a relatively large *PNCH* coupling and that the methyl group *trans* to the lone pair will have a relatively small *PNCH* coupling. This is consistent with couplings of *ca.* 3 and 14 Hz at 'low' temperatures. In general, it also appears that the low-field methyl signal in deuteriochloroform or in methylene chloride solution has the

TABLE 1

Variable-temperature ^{1}H n.m.r. data for compounds (1) [a]

	High temperature		Low temperature				
R^1, R^2, X, Y [b]	δ(NMe_2)	$^3J(P\cdots H)$ [c]/Hz	δ(NMe_2)	$^3J(P\cdots H)$ [c]/Hz	$\Delta\nu$ [d]/Hz	T_c/K	$\Delta G^{\ddagger}_{T_c}$/kcal mol^{-1}
Bu^t,Me,NMe_2,NMe_2	2.70	7.6	2.63, 2.76	2.3, 13.0	7.9	239	12.5
	2.68	8.1			*ca.* 8	*ca.* 193	*ca.* 9.5 [e]
Bu^t,Bu^t,NMe_2,NMe_2	2.73 [f]	7.0 [f]	2.69, 2.80 [f]	3.0, 12.2 [f]	5.5	327	17.6 [f]
	2.66	8.0	2.49, 2.57 [e]	2.4, 13.1 [e]	5.2	215	11.4 [e]
Bu^t,Me,NMe_2,Cl	2.69 [g]	8.1 [g]	2.67, 2.45 [g]	2.8, 12.9 [g]	12.6	280	14.5 [g]
Bu^t,Bu^t,NMe_2,Cl	2.68 [g]	8.3 [h]	2.71, 2.58 [g]	2.7, 13.6 [g]	7.4	319	16.9 [g]
Bu^t,Bu^t,NPr^i_2,Cl			0.94, 1.20 [h]	*h*	15.7	375	19.5 [h]
Bu^t,Bu^t,NEt_2,NEt_2	3.17 [e,i]	8.0				< 220 [e]	
Ph,Ph,NMe_2,NMe_2	2.78	8.4	2.52, 3.02	1.9, 12.9	30	252	12.6
	2.87	8.7				< 183 [e]	< 9
C_6H_4Cl-*p*,C_6H_4Cl-*p*,NMe_2,NMe_2	2.83	8.5	2.60, 3.10	2.3 13.0	30	253	12.6
	2.88	8.5				< 183 [e]	< 9
C_6H_4Me-*p*,C_6H_4Me-*p*,NMe_2, NMe_2	2.86	8.5	2.57, 3.05	2.6, 13.0	29	250	12.5
C_6H_4OMe-*p*,C_6H_4OMe-*p*,NMe_2, NMe_2	2.83	8.6	2.66, 3.11	2.0, 12.7	27	254	12.7
	2.88	8.9				< 183 [e]	< 9
Ph,Ph,NMe_2,Cl	2.91	9.0	2.83, 3.06	3.1, 13.8	14	260	13.4
Ph,Ph,NEt_2,NEt_2	3.28	8.0	3.09, 3.47	2.3, 13.3	23	272	13.8

[a] In $CDCl_3$ solution, unless otherwise stated. [b] Where two isomers are formed, the first is that with a 'low-field' ^{31}P shift.[10] [c] $|J(PNCH) + J(PNPNCH)|$, except when X ≠ Y, where it is $J(PNCH)$. [d] Assuming that *k* at $T_c = \pi\Delta\nu/2^{\frac{1}{2}}$, where $\Delta\nu$ is the shift in the absence of exchange. [e] In CH_2Cl_2 solution. [f] In C_6H_6 solution. [g] In toluene solution; $\Delta\nu$ was < 3 Hz in $CDCl_3$ solution where less accurate, but similar, $\Delta G^{\ddagger}_{T_c}$ values were obtained. [h] $CH(CH_3)_2$ signal, of which that at low field was broadest, indicating a larger coupling to phosphorus (although < 0.5 Hz) than the high-field signal. *CH* signals at δ 3.08 and 4.30 p.p.m. [$J(PNCH)$ 2.5 and *ca.* 15 Hz respectively]. All the measurements were in PhCl solution. [i] NCH_2, see text.

[12] A. Rauk, L. C. Allen, and K. Mislow, *Angew Chem. Internat. Edn.*, 1970, **9**, 400.

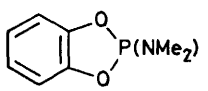
[13] O. J. Scherer and N. Kuhn, *Chem. Ber.*, 1974, **107**, 2123.

[14] G. Bulloch, R. Keat, and D. S. Rycroft, unpublished work.

largest coupling. The shift between the signals decreases in aromatic solvents and with (1; X = Cl, Y = NMe_2, R^1 = Bu^t, R^2 = Me or Bu^t) it is the upfield signal which has the largest coupling in toluene solution. Two *PNCH* couplings in a similar range appear in the 'low'-temperature spectra of (1; X = Y = NEt_2, R^1 = R^2 = Ph) and of (1; X = Cl, Y = NPr^i_2, R^1 = R^2 = Bu^t). In the latter compound the low-field isopropyl methyl signals were broader than the high-field methyl signals and ^1H-{^{31}P} decoupling showed that this was due to different couplings to phosphorus. ^1H-{^1H} Homonuclear decoupling also showed that the protons giving rise to the broadened methyl signals are coupled to the methine protons with the largest *PNCH* coupling, so that the largest *PNCCH* couplings may also arise from methyl groups *cis* to the phosphorus lone pair. The value of T_c for the latter compound was exceptionally high, leading to a P–N rotational barrier *ca.* 6 kcal mol^{-1} higher than in $PPhCl(NPr^i_2)$.[1,4]

The mean of the two *PNCH* couplings is equal to the coupling observed when rotation about the P–N bond is fast on the n.m.r. time scale in compounds (1; X = Cl, Y = NMe_2, R^1 = R^2 = Bu^t or Ph). This is not exactly true of the two couplings observed in the low-temperature spectra of the bis(dimethylamino)-derivatives (1; X = Y = NMe_2, R^1 = R^2 = alkyl or aryl). The dimethylamino-proton spectra of these derivatives form the X part of an $X_6AA'X'_6$ spin system (A = phosphorus, protons in bridging *N*-alkyl substituents being neglected), which will be a doublet enclosing a set of (often unresolved) signals when $|J(AX) + J(A'X)| < J(AA')$ [15] [*e.g.* see Figure (*c*)]. ^1H-{^{31}P} INDOR experiments of the type in ref. 16 indicate that $J(PNP)$ [$J(AA')$] is relatively small (<30 Hz) in these derivatives so that second-order effects are not very prominent when rotation about the P–N bonds is fast on the n.m.r. time scale and the apparent coupling, $J(PNCH)$, is 8—10 Hz. There are notable differences in the low-temperature spectra in that the signals with the large $P \cdots H$ coupling are fairly sharp, but the signals with the small coupling are poorly resolved.

The low-temperature apparent $P \cdots H$ couplings are smaller than those in $PPhCl(NMe_2)$ (19.2 and 6.7 Hz),[1] but similar to those in (C) (13.5 and 2.2 Hz).[8] It seems



(C)

likely that the apparent $P \cdots H$ couplings are not wholly dependent on the conformations of the dimethylamino-groups in (1). A possible contribution to these differences is suggested by the crystal structure of $[(Me_3Si)N{\cdot}P{\cdot}N(SiMe_3)_2]_3$ where the PNSi angles differ by 22.6° as a result of steric interactions.[9]

It was a tentative suggestion [10] that the large ^{31}P chemical-shift differences between the geometrical isomers of dialkylaminocyclodiphosphazanes have their origins in the different preferred conformations adopted by the amino-groups. This is not indicated, however, when the $P \cdots H$ couplings for the two isomeric forms of (1; X = Y = NMe_2, R^1 = R^2 = Bu^t) are compared (data are not available for other pairs of isomers).

A notable feature of the ^1H-{^{31}P} experiments is that the ^{31}P shifts are temperature dependent. An indication of this temperature dependence is given in Table 2.

TABLE 2

Temperature dependence of ^{31}P chemical shifts

(1) R^1, R^2, X, Y	δ_P(±0.2 p.p.m.) [a]	10^2 (Mean ^{31}P shift per °C) p.p.m.
Bu^t,Me,NMe_2,NMe_2	190.1 (−60), 192.3 (33)	2.4
	102.8 (−60), 105.7 (33)	3.1
Bu^t,Bu^t,NMe_2,NMe_2	180.3 (−65), 184.7 (33)	4.5
	91.5 (−65), 95.0 (33)	3.6
Bu^t,Me,NMe_2,Cl	138.6 (−60), 150.1 (60)	9.6, 3.2 [b]
Bu^t,Bu^t,NMe_2,Cl	128.8 (−40), 134.1 (60)	5.3
Bu^t,Bu^t,NEt_2,NEt_2	85.9 (−50), 91.3 (33)	6.5
Ph,Ph,NMe_2,NMe_2	162.0 (−56), 166.7 (50)	4.4 [c]
Ph,Ph,NMe_2,Cl	132.7 (−45), 139.6 (50)	7.3
Ph,Ph,NEt_2,NEt_2	158.4 (−32), 163.5 (50)	6.2
Bu^t,Me,Cl,Cl	225.3 (−56), 226.9 (107) [d]	1.0
$PPhCl(NMe_2)$	147.6 (−76), 146.2 (−20), 145.9 (25)	1.6 [e]
$PCl_2(NMe_2)$	162.4 (−56), 164.9 (33)	2.8
$P(NMe_2)_3$	120.9 (−56), 123.3 (33)	2.7

[a] Measured by ^1H-{^{31}P} double resonance in $CDCl_3$ solutions, unless otherwise stated. The temperature in °C is given in parentheses. [b] *P*Cl shift. [c] Other values for (1; R^1 = R^2 = C_6H_4Z-*p*, X = Y = NMe_2) are 4.0 (Z = Cl), 5.6 (Me), and 5.3 × 10^{-2} p.p.m. $°C^{-1}$ (OMe). [d] In toluene. [e] Upfield shift on increasing temperature.

The temperature variation is not linear, but the data are sufficient to show that in general those compounds with relatively high barriers to rotation about the exocyclic P–N bonds have the greatest dependence. The ^{31}P signals move upfield on lowering the temperature. Furthermore, in (1; X = Cl, Y = NMe_2, R^1 = Me, R^2 = Bu^t) the temperature dependence was greatest for the $P(NMe_2)$ signal. A smaller temperature dependence of ^{31}P shifts is generally shown by the acyclic aminophosphines in Table 2 and by the cyclodiphosphazane, (1; X = Y = Cl, R^1 = Me, R^2 = Bu^t) with no exocyclic amino-groups. Chloro(dimethylamino)phenylphosphine is unusual in that the ^{31}P signal moves to low field on lowering the temperature.

A possible reason for these changes is that the dialkylamino-group spends a greater proportion of time in a

[15] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.
[16] W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.

preferred conformation at low temperature when the strength of the exocyclic P–N bond is increased. The effect of changes in P–N bond strength on ^{31}P chemical shift is little understood, but it may be noted that increasing overall electron release to phosphorus in the series $PCl_{3-n}(NMe_2)_n$ ($n = 0$—3) results in an upfield ^{31}P shift.[17] As would be expected on this basis, the chemical-shift dependence is least at temperatures below those where coalescence is observed.

The ^{31}P chemical shifts are also affected by the solvent. For example, on passing from deuteriochloroform to benzene solution, shifts of up to 3 p.p.m. have been observed. Furthermore, the temperature dependence is, to a smaller extent, related to the solvent [at least for (1; X = Cl, Y = NMe_2, $R^1 = R^2 = Bu^t$) and (1; X = Y = NMe_2, $R^1 = R^2 = Bu^t$)]. These findings suggest that effects such as self association or solvent association will have to be taken into account,[18] but we do not believe that these make the major contribution to the temperature dependence of ^{31}P shifts.

The barriers to rotation of the dialkylamino-groups in compounds (1) are largely determined by steric effects. The cyclodiphosphazane ring appears to exert greater steric constraints than are common in acyclic aminophosphines. However, the reasons for the dramatic differences in barrier between a given pair of geometrical isomers are unclear. Cross-ring interactions between the dialkylamino-groups in the *cis* isomers would be expected to destabilise conformations such as that in (B), thus lowering the barrier. Against this, it may be noted that the isomers with the highest barriers ($R^1 = R^2$ = alkyl or aryl) are those which have been tentatively assigned *cis* structures.[10] Further progress will be possible when more definite structural assignments have been made for both series of compounds.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were obtained as previously described [10,19] under conditions of complete ^{31}P decoupling. The dimethylamino-proton spectra thus showed the collapse of two equal-intensity uncoupled singlets so that the calculation of $\Delta G^{\ddagger}_{T_c}$ using the relation $\Delta G^{\ddagger}_{T_c} = T_c[45.63 + 4.58 \log_{10}(T_c/\Delta\nu)]$ cal mol^{-1} is a valid procedure.[11] Errors (± 0.3 kcal mol^{-1}) arise mainly from temperature measurements; calibration was by the method involving measurement of the shifts of methanol or ethylene glycol signals. The calculation of $\Delta G^{\ddagger}_{T_c}$ for the diethylamino- and di-isopropylamino-derivatives introduces a larger error (*ca.* 0.5 kcal mol^{-1}). The temperature dependence of ^{31}P chemical shifts was investigated with the spectrometer operating in the external-lock mode in order to eliminate effects due to the temperature dependence of the lock signal.

Cyclodiphosphazanes and aminophosphines were prepared as previously described,[10] except as indicated below.

2-Chloro-4-di-isopropylamino-1,3-di-t-butylcyclodiphosphazane.— 2,4-Dichloro-1,3-di-t-butylcyclodiphosphazane (3.5 g, 12.7 mmol) in benzene (40 cm^3) was mixed with di-isopropylamine (7.7 g, 76.2 mmol) and sealed in a thick-walled glass tube. The tube was heated (18 h) at 130 °C. Di-isopropylamine hydrochloride (1.6 g, 11.6 mmol) was removed and the filtrate was evaporated to dryness. The residue was extracted with hot light petroleum (25 cm^3, b.p. 40—60 °C) to give a white solid, which on crystallisation from benzene gave the *compound* (3.6 g, 83%), m.p. 162 °C (Found: C, 49.2; H, 9.9; N, 12.3%; *m/e* 339. $C_{14}H_{32}{}^{35}ClN_3P_2$ requires C, 49.5; H, 9.4; N, 12.4%; *m/e* 339). Phosphorus-31 n.m.r. spectrum in CH_2Cl_2: δ 184.0 (*P*Cl) and 114.5 p.p.m. [$^2J(PNP)$ 30 ± 2 Hz] (for ^1H n.m.r. data see Table 1). There was no evidence to suggest the formation of any 2,4-bis(di-isopropylamino)-1,3-di-t-butylcyclodiphosphazane.

A further experiment in which the above mono(di-isopropylamino)-derivative was heated with excess of di-isopropylamine in a sealed tube at 175 °C for 11 d led to extensive decomposition of the starting material. When the reaction was carried out in refluxing diethyl ether solution (15 h) a mixture of starting material and the mono-(di-isopropylamino)-derivative (*ca.* 1 : 1) was obtained.

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