Nuclear Magnetic Resonance Investigation of Rotation about Phosphorus(V)–Nitrogen Bonds in Aminocyclodiphosph(V)azanes

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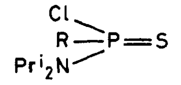
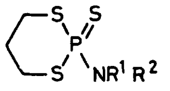
Hydrogen-1 n.m.r. data on the cyclodiphosph(V)azanes $R_2N(X)PNBu^tP(X)(NR_2)NBu^t$ (R = Me, X = O, S, or Se; R = Et, X = S or Se) and $Me_2N(O)PNRP(O)(NMe_2)NR$ (R = Ph or CH_2Ph) indicate that rotation about the *exo* P^V–N bonds is slow on the n.m.r. time scale at ambient or sub-ambient temperatures. In the former series, *trans* isomers have higher rotational barriers, $\Delta G_{T_c}^{\ddagger}$, than analogous *cis* isomers and these barriers are also greater for *trans* oxides than analogous sulphides or selenides. The rotational barriers for P^V–N and P^{III}–N have also been measured for the compounds $Me_2NPNBu^tP(X)(NMe_2)NBu^t$ (X = S, Se, or MeI), $Me_2N(X)PNBu^tP(Y)(Cl)NBu^t$ (X = S, Y = lone pair; X = O, Y = O), and *cis*-$Me_2N(S)PNBu^tP(Se)(NMe_2)NBu^t$. Carbon-13 n.m.r. data obtained at various temperatures on geometrical isomers of $Me_2N(X)PNBu^tP(NMe_2)(X)NBu^t$ (X = O, S, or Se) indicate that *J*(*P*N*C*) (*exo*) is much more stereospecific than *J*(*P*NC*H*), especially when X = S or Se.

THE measurement of rotational barriers for tervalent phosphorus–nitrogen, P^{III}–N, bonds by ^1H n.m.r. spectroscopy has been widely reported (see refs. 1—4 for a recent summary), although the factors which determine the magnitude of these barriers have not been clearly identified. Rotational barriers about quinquevalent phosphorus–nitrogen, P^V–N, bonds (four-co-ordinate phosphorus) are generally lower than for analogous P^{III}–N bonds and their measurement so far has been limited to compounds (1) [1] and (2) [5] where the amino-group has relatively bulky i-propyl or t-butyl substituents.

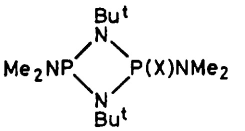


(1) (R = Me or Ph)

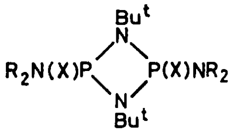


(2) (R^1, R^2 = Bu^t, Pr^i; Pr^i, Pr^i; or Bu^t, Me)

The effects of restricted rotation about P^V–N bonds at five-co-ordinated phosphorus have also been recognised,[6] but they are often complicated by other exchange processes such as pseudorotation. It has also been reported [7] that there is restricted rotation about the P–N bond in the phosphetidine, $Me_2CCHMeCMe_2P(O)NMe_2$, at ambient temperatures, but this claim requires further authentication to exclude other possibilities such as isomerisation. We now report on a study of rotation about the *exo* P^V–N bonds in the cyclodiphosphazanes (3) (X = S, Se, or MeI) and (4) (R = Me, X = O, S, or Se; R = Et, X = S or Se) and related compounds.[8]



(3)



(4)

In most cases geometrical isomers, arising from the different orientations of the *exo*-phosphorus substituents with respect to the P_2N_2 ring, were available.[9] Coalescence phenomena, recorded from the ^1H n.m.r. spectra, have been used to obtain the free energy of activation, $\Delta G_{T_c}^{\ddagger}$, for the rotation process at the coalescence temperature. Carbon-13 n.m.r. data have also been obtained for the compounds (4) (R = Me).

RESULTS AND DISCUSSION

The dimethylamino-proton signals in the ambient-temperature ^1H n.m.r. spectrum of *trans*-(4) (R = Me, X = O) were broadened, indicating the operation of an exchange process at an intermediate rate on the n.m.r. time scale. This was confirmed by the spectra obtained at various temperatures (Figure 1). Although the dimethylamino-proton signals are 'deceptively simple' as a result of the magnetic inequivalence of the ^{31}P nuclei (*e.g.* see ref. 10), complete ^{31}P decoupling showed that two signals of equal intensity could be obtained at sub-ambient temperatures. The changes in appearance of these signals with temperature readily gave $\Delta G_{T_c}^{\ddagger}$ (see below). The ^1H n.m.r. spectra of the other cyclodiphosphazanes in Table 1 showed similar behaviour,

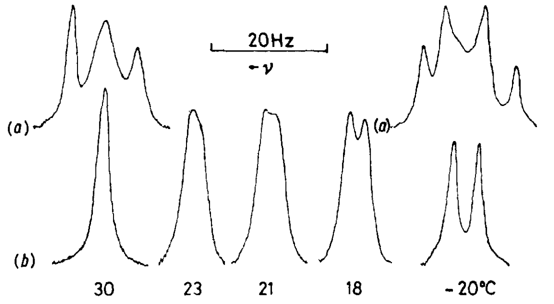


FIGURE 1 Variable-temperature ^1H n.m.r. spectra of *trans*-(4) (R = Me, X = O) showing N-methyl signals only, (*a*) normal, (*b*) with ^{31}P decoupling

although the coalescence point was often observed at lower temperatures.

TABLE 1

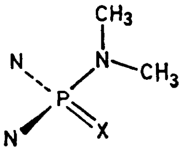
Variable-temperature ^{1}H n.m.r. data [a]

Compound	High temperature $\delta(NMe_2)$ /p.p.m.	High temperature $J(PNCH)$ [b] /Hz	Low temperature $\delta(NMe_2)$ /p.p.m.	Low temperature $^3J(PNCH)$ [b] /Hz	$\Delta\nu$ [c] /Hz	T_c /K	$\Delta G_{T_c}\ddagger$ [d] /kcal mol^{-1}
cis-(4) (R = Me, X = O)	2.72	10.5	2.72 2.76	10.5 9.1	2.6	213	11.6
trans-(4) (R = Me, X = O)	2.78	10.8	2.76 2.83	11.5 9.5	4.3	294	15.9
cis-(4)(R = Me, X = S)	2.93	11.8	2.89 2.95	10.0 13.7	3.7	219	11.8
trans-(4) (R = Me, X = S)	2.92	12.0	2.88 2.95	11.3 13.4	4.1	256	13.8
cis-(4) (R = Me, X = Se)	2.92	12.8	2.90 2.98	10.0 15.1	4.6	224	12.0
trans-(4) (R = Me, X = Se)	3.01	12.8	2.99 3.05	11.0 14.8	3.3	248	13.5
cis-$Me_2N(S)PNBu^tP(Se)(NMe_2)NBu^t$	2.94 (S)	12.3	2.86 2.92	11.0 13.7	3.8	226	12.1 (S)
	2.97 (Se)	12.8	2.87 2.95	10.8 14.8	4.6	215	11.5 (Se)
cis-(3) (X = S)	2.64 (P^{III})	9.0	2.56 2.68	1.9 13.3	7.5	282	14.9 (P^{III})
	2.90	11.6	*e*	*e*	*e*	<183	<9
trans-(3) (X = S)	2.69 (P^{III}) [f]	8.7	2.54 [f] 2.69 [f]	14.3 3.4	9	352 [f]	18.6 (P^{III})
	2.69 [f]	11.6	2.23 [f] 2.89 [f]	10.5 12.4	40	295 [f]	14.6
cis-(3) (X = Se)	2.68 (P^{III})	8.8	2.63 2.77	3.2 13.7	8.2	301	15.9 (P^{III})
	2.99	12.0	*e*	*e*	*e*	<183	<9
trans-(3) (X = Se)	2.72 (P^{III}) [f]	8.6	2.53 [f] 2.75 [f]	13.9 3.0	13	349 [f]	18.2 (P^{III})
	2.72 [f]	11.6	2.25 [f] 2.91 [f]	10.1 13.1	40	286 [f]	14.2
cis-(4) (R = Et, X = S)	3.40 [g]	14.0	3.26 3.45	*e* *e*	11.3	256	13.3 (±0.5)
cis-(4) (R = Et, X = Se)	3.41 [g]	14.4	3.27 3.49	*e* *e*	13.1	263	13.6 (±0.5)
$[Me_2N(O)PNPh]_2$	2.87	11.1	2.66 3.08	*ca.* 12 *ca.* 9	25.5	197	9.8
$[Me_2N(O)PCH_2Ph]_2$	2.85	11.1	*e*	*e*	*e*	<177	<9
cis-(3) (X = MeI)	2.48 (P^{III}) [f]	8.8	2.34 [f] 2.45 [f]	1.7 15.4	6.3	323 [f]	17.3 (P^{III})
	3.02	11.3	2.92 2.94	9.7 12.3	1.4	216	12.0 (±0.5)
trans-(3) (X = MeI)	2.72 (P^{III}) [h]	8.8	2.55 [h] 2.72 [h]	3.4 14.3	10.3	336 [h]	17.7 (P^{III})
	2.79 [h]	10.5	2.71 3.06	10.0 11.4	20.8	312	15.9
$Me_2N(S)PNBu^tP(Cl)NBu^t$ [i]	2.88	12.1	2.84 2.94	11.1 12.8	6.0	225	11.9
$Me_2N(S)PNBu^tP(Cl)NBu^t$	2.60 [f]	11.1	2.18 [f] 2.78 [f]	10.7 13.4	36.1	333 [f]	16.7
$Me_2N(O)PNBu^tP(O)(Cl)NBu^t$ [j]	2.74	11.9	2.63 2.79	13.1 ± 1 10.2 ± 1	9.4	264	13.8
$Me_2N(O)PNBu^tP(O)(Cl)NBu^t$	2.70 [f]	*ca.* 11	2.52 [f] 2.67 [f]	11.7 ± 1 10.3 ± 1	8.9	331 [f]	17.5

[a] In $CDCl_3$ or CH_2Cl_2 solution, unless otherwise stated. [b] $|^3J(PNCH) + {}^5J(PNPNCH)|$, for symmetrical dialkylaminocyclodiphosphazanes. [c] Assuming that $k = \pi\Delta\nu/\sqrt{2}$ at T_c, where $\Delta\nu$ is the difference in chemical shift in the absence of exchange. [d] Errors are ±0.3 kcal mol^{-1}, unless otherwise stated. [e] Not measured. [f] In C_6H_5Cl solution. [g] $\delta(NCH_2)$. [h] In Me_2SO solution. [i] Isomer with $\delta[P(S)NMe_2] = 63.3$ (ref. 9). [j] Isomer with $\delta[P(O)NMe_2] = 0.3$ (ref. 9).

Comparison of the $\Delta G_{T_c}\ddagger$ data in Table 1 enables the nature of the rate process to be defined with a good degree of certainty. This is a generally accepted procedure, provided that the same type of rate process is compared in each case. Thus, the replacement of dimethylamino- by diethylamino-groups [compare *cis*-(4) (R = Me, X = S or Se) with *cis*-(4) (R = Et, X = S or Se)] results in an increase in $\Delta G_{T_c}\ddagger$, as does an increase in the bulk of the *endo*-N-substituent {compare *cis*- or *trans*-(4) (R = Me, X = O) with $[Me_2NP(O)NCH_2Ph]_2$ or $[Me_2NP(O)NPh]_2$}. These trends are best associated with a rate process involving rotation about the *exo* P–N bond rather than inversion at endo- or exo-cyclic nitrogen atoms. *X*-Ray crystallographic studies (below) in any case show the nitrogen atoms to be essentially planar. Interconversion of geometrical isomers can also be ruled out since separate signals can be observed for mixtures of isomers over the whole temperature range examined. Similar observations were made for analogous cyclodiphosph(III)azanes.[2]

The observation of chemically shifted dimethylamino-proton signals when the rate process is slow on the n.m.r. timescale is consistent with the preferred conformation of the dimethylamino-groups being that shown in (5). A planar or near planar distribution of bonds about the *exo*-nitrogen atom is assumed from the results of *X*-ray crystallographic studies. Conformation (5) is found[8,11] in the crystal structure of *cis*-(4) (R = Me, X = S), in which the molecule has close to C_{2v} symmetry. The planes containing the NC_2 atoms are twisted away from the vertical plane of symmetry by 5°, evidently by a cross-ring steric interaction. Little is known of the preferred conformations of unhindered P^V–N bonds, although a common feature of the many crystallographic studies[12-19] of relevant phosphorus–chalcogens is that the plane containing the bonds to nitrogen also contains the phosphorus–chalcogen bond, *i.e.* N–C and P=X bonds are eclipsed as in (5) and the nitrogen lone pair is orthogonal to the phosphorus–chalcogen bond. Related conformations are also obtained in aminocyclophosphazenes where the amino-nitrogen lone pair is generally orthogonal to the *endo* P–N bonds, except when competition from other exocyclic π donors is encountered.[20,21] *Ab initio* calculations[22,23] indicate that the conformation adopted about a P^V–O bond (bridging oxygen) is dependent on interactions between oxygen lone pairs and the antibonding orbitals associated with other bonds to phosphorus (primarily by an antiperiplanar $n \rightarrow \sigma^*$ interaction); this type of interaction may well be relevant to the conformations of phosphorus(V)–nitrogen compounds also.



(5)

The spin-coupling constants *J*(*P*NC*H*) and *J*(*P*N*C*) are also of considerable interest in connection with possible stereospecific contributions.[24] The outer components of the dimethylamino-proton ' triplets ' in the spectra of *trans*-(4) (R = Me, X = O) (Figure 1) are separated by $|J(PNCH) + J(PNPNCH)|$,[10] a close approximation to *J*(*P*NC*H*). The two *P*NC*H* couplings for this compound are therefore similar in magnitude, and have the same relative sign because their mean (10.5 Hz) is close to the *P*NC*H* coupling that is obtained at elevated temperatures (*ca.* 10.8 Hz). This is a general observation for the compounds (4), which differs from the analogous tervalent phosphorus compounds[2] where the two couplings are, for example, *ca.* 2.3 and 13.0 Hz in $cis\text{-Me}_2\text{N}\overline{\text{PNBu}^{t}\text{P(NMe}_2\text{)N}}\text{Bu}^{t}$. Large differences in *J*(*P*NC*H*) have also been detected in acyclic P^{III}–N compounds,[1] and the larger coupling can be assigned to the methyl group *cis* to the phosphorus lone pair.[24] The two *P*NC*H* couplings in the compounds (4) do, however, differ by increasing amounts in the series X = O ⟶ S ⟶ Se, but it is difficult to decide which coupling corresponds to the methyl group *cis* to the chalcogen atom. There is evidence to suggest that the proton signals from a methyl group close to a phosphoryl-oxygen atom will be deshielded,[25] and on this basis the smaller couplings in (4) (R = Me, X = O) could be assigned to the methyl group *cis* to oxygen. On the other hand, the sulphides and selenides (4) (R = Me, X = S or Se) have smaller couplings to the high-field N-methyl protons. The chalcogen derivatives, $P_4(NMe)_6X_4$ (X = O,[26] S,[27] or Se[27]), where the N–C bonds are close to eclipsing the phosphorus–chalcogen bonds,[28] have apparent *P*NC*H* couplings of 9.6, 13, and 14 Hz respectively (complications arise from the magnetic inequivalence of the ^{31}P nuclei). A tentative conclusion for the sulphides and selenides (4) is therefore

TABLE 2

Carbon-13 n.m.r. data[a]

	N*C*H$_3$ Signals						C*C*H$_3$[c] Signals	
Compound	θ$_c$/°C	δ(C)	$^2J(PNC)$[b] /Hz	θ$_c$/°C	δ(C)	$^2J(PNC)$[b] /Hz	δ(C)	$^2J(PNCC)$ /Hz
cis-(4) (R = Me, X = O)	*d*	37.5	5.3	−90	37.3[e] 37.5	*ca.* 7 *ca.* 2.5	29.8	*f*
trans-(4) (R = Me, X = O)	70	36.5	*ca.* 5	−40	36.5 36.7	5.9 6.1	30.0	4.4
cis-(4) (R = Me, X = S)	*d*	38.6	6.2	−60	37.3 39.3	<1 11.6	28.9	4.5
trans-(4) (R = Me, X = S)	60	38.2	5.2	−50	36.9 38.8	<1 10.3	30.1	4.6
cis-(4) (R = Me, X = Se)	*d*	38.9	5.8	−60	37.0 40.1	<1 12.6	28.6	*f*
trans-(4) (R = Me, X = Se)	60	*ca.* 39	*f*	−60	36.7 39.9	<1 12.0	30.2	4.5

[a] In $CDCl_3$ solutions at the temperatures given. [b] $|^2J(PNC) + {}^4J(PNPNC)|$. [c] The quaternary C was a singlet in the range δ 53—56. [d] Ambient temperatures (*ca.* 25 °C). [e] $CDCl_3$—CD_2Cl_2 mixture. [f] Broadened signals.

that the larger coupling arises from the methyl group *cis* to the chalcogen.

The N-methyl ^{13}C signals for the compounds (4) (Table 2) constitute the X part of an AA'X spin system (A,A' are ^{31}P nuclei, isotope effects being ignored), the characteristics of which are well documented.[29] $|J(PNCH) + J(PNPNC)|$ is readily obtained from the outer intense doublet and it is assumed that $J(PNPNC)$ is small (<1 Hz). Spectral analysis showed the latter coupling was 0.1 Hz in *trans*-(4) (R = Me, X = Se) with a sign opposite to that of $J(PNC)$. The two NCH$_3$ signals obtained when rotation about the *exo* P–N bond is slow show that $J(PNC)$ is generally more stereospecific than $J(PNCH)$, especially when X = S or Se. This is clearly shown in Figure 2; off-resonance ^{13}C-{^{1}H} experiments also showed that in *trans*-(4) (R = Me, X = O or Se) smaller $J(PNC)$ couplings are associated with smaller $J(PNCH)$ couplings. Comparison of the low-temperature values with the high-temperature average demonstrates that there is no change in sign of $J(PNC)$ and since this coupling is +3.4 and +3.3 Hz in P(NMe$_2$)$_3$X (X = O and S respectively),[30] it is likely that all the observed couplings are positive. Consistent with this, we have used ^{13}C-{^{1}H} off-resonance experiments to show that $J(PNC)$ and $J(PNCH)$ have the same sign in *cis*-(4) (R = Me, X = O) at high temperatures, and that the same relationship holds for the low-field NCH$_3$ signal in *trans*-(4) (R = Me, X = Se). Geometrical isomerism had a significant influence on the stereospecificity of $J(PNC)$ only in the case of (4) (R = Me, X = O), being non-specific in the *trans* isomer, but assuming values of *ca.* 7 and *ca.* 2.5 Hz in the *cis* isomer. These results do not parallel those obtained[31] for PRCl(NPr$^i_2$)S (R = Me or Ph) where $J(PNC)$ was ⩽ 3Hz and no evidence was obtained for stereospecific couplings, although $J(PNCC)$ was <3 and 7 Hz at low temperatures in the latter acyclic compounds.

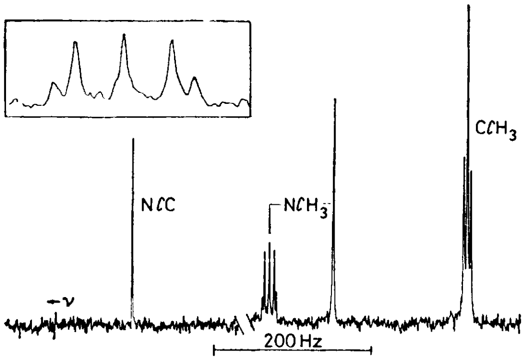


FIGURE 2 ^{13}C-{^{1}H} n.m.r. spectrum (0.25 Hz per data point) of *trans*-(4) (R = Me, X = Se) at −60 °C, with, inset, a 10 × horizontal expansion of the low-field NCH$_3$ signals

This work, and that reported previously,[1,5] clearly indicates that steric effects play an important role in determining the magnitude of the rotational barriers for P^{V}–N bonds. The discovery that *cis* isomers (4) have lower rotational barriers than the corresponding *trans* isomers can be rationalised in terms of a cross-ring steric interaction in the *cis* isomers destabilizing the ground-state conformation relative to the transition state for the rotation process. When the phosphorus substituents are the same, this provides a good method of distinguishing geometrical isomers. In addition, it is possible, to identify for the first time significant differences in rotational barriers caused by changes in the chalcogen atoms. This is most noticeable in the *trans* isomers of (4), presumably where the barrier is not dominated by a cross-ring steric interaction, and the barriers decrease in the order X = O > S ⪆ Se. Whilst the differences between the sulphides and selenides are not outside the range of experimental error, the barriers for the sulphides are always calculated to be higher, including *cis*-Me$_2$N(S)PNBu^{t}P(Se)(NMe$_2$)NBu^t, which provides a more direct comparison. The rotational barriers appear to be inversely related to the size of the chalcogen atom, so that steric interactions between the latter atom and the dimethylamino-groups are not important. On the other hand, a shortening of the *exo* P–N bonds in compounds (4) might be expected to increase N-methyl–C-methyl interactions and lead to a higher rotational barrier. There are few accurate data with which to compare analogous P(S)–N and P(O)–N bonds, but in the compound Cl$_2$P(O)NPhP(S)Cl$_2$, *X*-ray crystallography[32] shows that the latter bond is significantly shorter. The data in Table 1 also show that in both the *cis* and *trans* mixed-oxidation-state compounds (3) (X = S, Se, or MeI) rotational barriers are higher for P^{III}–N bonds than for P^{V}–N bonds as expected.[1,2] Also, for both P^{III}–N and P^{V}–N bonds the barriers in the *trans* isomers are higher than in the *cis* isomers. These can be compared with the barriers for the P^{III}–N bonds in *cis*- and *trans*-(4) (R = Me, X = lone pair) where $\Delta G_{T_c}^{\ddagger}$ is 11.4 and 17.6 kcal mol^{-1} respectively.[2,] *

The configurations of Me$_2$N(S)PNBu^{t}P(Cl)NBu^t and Me$_2$N(O)PNBu^{t}P(O)(Cl)NBu^t, the last four compounds in Table 1, are not known and, unfortunately, differences in $\Delta G_{T_c}^{\ddagger}$ are not readily interpreted in terms of *cis* or *trans* isomers. The isomeric differences are similar to those for the other compounds and it seems reasonable to assign the lower barriers to the '*cis*' compounds even though cross-ring steric interactions are presumably less important when chloride replaces dimethylamino. However, the effect of this substitution if this assignment *is* made is to increase the barrier in all cases and it would be consistent with the operation of a configurationally non-specific electronic effect.

EXPERIMENTAL

The preparation of the compounds has been reported previously.[9,33] Hydrogen-1 n.m.r. spectra were obtained on a JEOL C60 HL spectrometer at 60 MHz and coalescence

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* Throughout this paper: 1 cal = 4.184 J.

phenomena were investigated under conditions of complete ^{31}P decoupling. The relationship $\Delta G_{T_c}^{\ddagger} = T_c$ $(45.67 + 4.58 \log T_c/\Delta\nu)$ (T_c = coalescence temperature, $\Delta\nu$ = shift in Hz in the absence of exchange) is valid under these conditions.[2,34] Temperatures were calibrated using the shifts of methanol or ethylene glycol. Carbon-13 n.m.r. spectra were obtained on a Varian XL-100-12 spectrometer at 25 MHz in the pulsed Fourier-transform mode.

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