Dynamic Nuclear Magnetic Resonance Investigation of Phosphonamidothioic and Phosphonamidous Chlorides [1]

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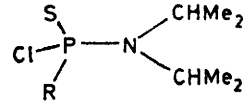
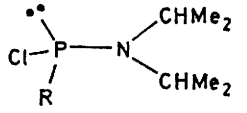
NN-Di-isopropyl-*P*-alkylphosphonamidothioic chlorides, $RP(S)(Cl)NPr^{i}_{2}$ (R = Me, Bu^{t}, or Ph), show non-equivalent *N*-isopropyl groups in the proton n.m.r. spectra at low temperature. The barriers to isopropyl site-exchange have been determined by iterative bandshape analysis and lie in the range 9—12.6 kcal mol^{-1}. These data are believed to refer to P–N bond rotation though alternative explanations are also considered. The corresponding *NN*-dimethyl compounds do not show any *N*-methyl non-equivalence at low temperature. Barriers to P–N bond rotation in some analogous phosphonamidous compounds, $R^{1}P(Cl)–NR^{2}_{2}$ have also been measured and are discussed in conjunction with literature data. The P–N rotational barriers generally increase with the steric bulk of the alkyl substituents, though the *NN*-dimethyl compounds show an unusual inverse steric effect of the *P*-alkyl substituent. The *P*-t-butyl compounds do not show any evidence of restricted rotation around the phosphorus–carbon bond at low temperature (−100 to −150 °C).

THE dynamic stereochemistry of aminophosphines has been extensively studied by n.m.r. spectroscopy in several laboratories, particularly those of Simonnin,[2,3] Cowley and Dewar,[4-6] Friebolin,[7] and Goldwhite.[8,9] Attention has centred on the phosphorus–nitrogen rotation barriers as these can be fairly large if the phosphorus atom bears a halogen substituent; for example the barrier in *NN*-dimethyl-*P*-phenylphosphonamidous chloride, $C_6H_5P(Cl)-NMe_2$, is 10.8 kcal mol^{-1}. The P–N rotation barrier was found to be raised on increasing the bulk of the *N*-alkyl substituents.[6,7,9] There has been considerable discussion in the literature regarding the possible involvement in the torsional process of $(p–d)_\pi$ bonding and repulsive interactions between vicinal lone pairs of electrons.

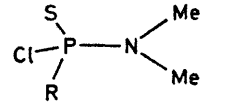
Aminophosphine sulphides and oxides on the other hand have received little attention, though it has been reported that the ^{1}H n.m.r. spectra of the phosphonamidic chlorides $C_6H_5P(O)(Cl)-NMe_2$, $Pr^{i}P(O)(Cl)-NMe_2$,



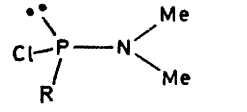
(1) R = Me
(2) R = Ph
(3) R = Bu^{t}



(4) R = Me
(5) R = Ph
(6) R = Bu^{t}



(7) R = Ph
(8) R = Bu^{t}



(9) R = Me
(10) R = Ph
(11) R = Bu^{t}

and $ClCH_2P(O)(Cl)-NMe_2$ remained unchanged down to −80 or −100 °C.[2,8] These observations suggest that the P–N torsional barrier in these compounds is less than *ca.* 8 kcal mol^{-1}. We now report on a low temperature

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[2] M. P. Simonnin, J. J. Basselier, and C. Charrier, *Bull. Soc. chim. France*, 1967, 3544.
[3] M. P. Simonnin, C. Charrier, and R. Burgada, *Org. Magnetic Resonance*, 1972, **4**, 113.
[4] A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, 1968, **90**, 4185.
[5] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.
[6] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206.
[7] D. Imbery and H. Friebolin, *Z. Naturforsch.*, 1968, **23b**, 759.
[8] H. Goldwhite and D. G. Rowsell, *Chem. Comm.*, 1969, 713.
[9] D. DiStefano, H. Goldwhite, and E. Mazzola, *Org. Magnetic Resonance*, 1974, **6**, 1.

n.m.r. investigation of some phosphonamidothioic chlorides and their corresponding phosphonamidous chlorides.

RESULTS

The *NN*-di-isopropylphosphonamidothioic chlorides (1)—(3) show two isopropyl methyl doublets [^3J(HCCH) *ca.* 6.8 Hz] in the ^{1}H n.m.r. spectrum at ambient temperature. The two NCH hydrogens are isochronous and show a doublet of septuplets due to vicinal coupling to the phosphorus atom and to the methyl groups. The two *N*-isopropyl groups are therefore equivalent, and the two doublets arise from geminal nonequivalence of the methyl groups owing to the absence of a molecular symmetry plane through the prochiral methine carbon atoms.[10] On lowering the sample temperature the two methyl doublets collapsed and eventually separated into four doublets of equal intensity. In the same temperature range, the NCH multiplet also broadened and separated into a more complex set of signals. Clearly the isopropyl groups have become non-equivalent on the n.m.r. time-scale at low temperature (probably due to slow rotation around the P–N bond, see Discussion section). The rate process involves a number of sites, therefore the rate constant cannot be determined accurately with a simple analytical equation, and a computer must be used to analyse the exchange modified bandshape. Since the spectra are close to first order, the components of the methyl doublets may be treated as individual sites within the multisite approach of Anderson,[11] Kubo,[12] McConnell,[13] and Sack.[14] The total magnetisation (G) at frequency ν for the general n-site case is given by equation (1) where C is a

$$G = -iC[P_j][A_{jk}]^{-1}[1] \qquad (1)$$

constant, P_j is a row vector containing the n equilibrium site intensities, [1] is a column vector of units, and A_{jk} is an $n \times n$ complex matrix containing the following elements: $A_{jk} = -R_{jk}$ (where $j \neq k$) and

$$A_{jj} = -2\pi i(\nu_j - \nu) + 1/T_j + \sum_{\substack{k=1 \\ k \neq j}}^{n} R_{jk}$$

where R_{jk} are the rate constants (in s^{-1}) for transition from site j to site k, ν_j are the signal positions (in Hz), T_j are the traverse relaxation times ($1/\pi \times$ linewidth), and $i = (-1)^{\frac{1}{2}}$.

A computer program based on these equations was originally devised by Saunders [15] in his elegant study of the bullvalene rearrangement, and similar programs have been developed by other investigators.[16] Exchange rates are usually estimated by visually searching for a calculated line shape that closely resembles the experimental spectrum. However, Gutowsky and his co-workers [17] have reported using an iterative procedure for deriving the exchange rate directly from the experimental spectrum in the coupled two-site case. This approach offers significant advantages for bandshape analysis. (i) Visual searching for a calculated bandshape resembling the experimental spectrum is a very subjective procedure and inexperienced analysts may tend to concentrate on one particular feature of the spectrum at the expense of others. However, it is possible *partly* to alleviate this problem by arranging for the calculated bandshapes to be plotted on the same scales as the experimental spectrum. Iterative fitting of the whole bandshape using a least squares criterion removes the subjective element, though if the standard deviation is not satisfactory the analyst may alter another spectral parameter (*e.g.* the position of a signal) to improve the fit. (ii) Iterative fitting is usually much faster and avoids generating large amounts of unnecessary graphical computer output.

The iterative approach has been used in the present investigation by extending it to the general multisite case.* In the resulting program (INMR), the site exchange rate is varied over a range to afford the optimum agreement (as determined by the method of least squares) between calculated and experimental spectra (the latter is supplied in digital form). Theoretical spectra are calculated in a subroutine based on the approach of Saunders.[15] The required absorption mode signal intensity (G_ν) at frequency ν is given by the imaginary part of equation (1). This can be extracted simply and is given in equation (2), thus avoiding the need to handle complex matrices. In equation

$$G_\nu = C[P_j][B_{jk} + 4\pi^2(\nu_j - \nu)(\nu_k - \nu)B_{jk}^{-1}]^{-1}[I] \qquad (2)$$

(2) $B_{jk} = -R_{jk}$ (where $j \neq k$) and

$$B_{jj} = 1/T_i + \sum_{\substack{k=1 \\ k \neq j}}^{n} R_{jk}$$

Input to INMR consists of the experimental spectrum in digital form, site positions, relative intensities, linewidths, relative transition probabilities, and an estimated value of the rate constant. The program automatically varies the latter from half to twice the initial value to afford the best fit (method of least squares) of the calculated to the experimental lineshape (see Figure 1). Analysis is speeded up by first varying the rate constant in 10% steps to locate the appropriate range and then in 2% steps. The time required to process an 8 site case of 50—100 spectral points is *ca.* 1 min on an ICL-1906A computer (cases of 2—4 sites require only a few seconds).

Small second-order effects on the relative intensities of the doublet components in compounds (1)—(3) were accommodated in the computer input. Line positions in the slow exchange region were not significantly temperature dependent and these values were used throughout the exchange broadened region as they provided satisfactory spectral fits (Figure 1). Linewidths were determined relative to tetramethylsilane as a reference (the solvent signal provided the internal field-frequency lock). In compounds (3) and (6) the t-butyl signals [d, ^3J(PCCH) 21.5 and 15.0 Hz respectively] overlapped the isopropyl methyl signals and made

* Reeves and his co-workers have independently reported using iterative lineshape fitting in multisite exchanging systems: L. W. Reeves, R. C. Shaddick, and K. N. Shaw, *Canad. J. Chem.*, 1971, **49**, 3683; S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, 1973, **95**, 670. The latter programs also have provision for other parameters to be optimised in addition to the exchange rate.

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[11] P. W. Anderson, *J. Phys. Soc. Japan*, 1954, **9**, 316.
[12] R. Kubo, *J. Phys. Soc. Japan*, 1954, **9**, 935.
[13] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.
[14] R. A. Sack, *Mol. Phys.*, 1958, **1**, 163.
[15] M. Saunders, *Tetrahedron Letters*, 1963, 1699; M. Saunders in 'Magnetic Resonance in Biological Systems,' eds. A. Ehrenberg, B. G. Malmstrom, and T. Vanngard, Pergamon Press, Oxford 1967, p. 85.
[16] For reviews on bandshape analysis in exchanging systems see (*a*) C. S. Johnson, *Adv. Magnetic Resonance*, 1965, **1**, 33; (*b*) L. W. Reeves, *Adv. Phys. Org. Chem.*, 1965, **3**, 187; (*c*) G. Binsch, *Topics Stereochem.*, 1968, **3**, 97.
[17] J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, 1965, **42**, 3396.

TABLE 1

Spectral data and free energy barriers for bond rotation in phosphonamidothioic and phosphonamidous chlorides

Compound	Solvent	T/°C	δ_{Me}[a]/ p.p.m.	$^3J_{Me}$[b]/Hz	δ_R[c]/ p.p.m.	J_R[d]/Hz	T_C[e]/°C	k/s^{-1}	$\Delta G^{\ddagger}$[f]/ kcal mol^{-1}	Ref.
(1)	$CHCl_2F$	−100	1.13, 1.17, 1.45, 1.50	6.8	2.36	14.4	−66	62	10.3	*g*
(2)	$CHCl_2F$	−95	0.94, 1.22, 1.74, 1.78	6.8			−65	112	10.1	*g*
(3)	$CHCl_2F$	−72	1.29, 1.29, 1.54, 1.69	6.9	1.40	21.5	−29	27	12.6	*g*
(4)	[$^2H_8$]Toluene	−60	0.62, 0.95, 1.02, 1.26	6.8	1.40	13.3	−8	27	13.7	*g*
	CH_2:CHCl	<−20	*l*	*l*	*l*	*l*	−20	*l*	13.4	*h*
(5)	CCl_3F	−50	0.83, 1.11, 1.37, 1.45	6.7			−15	70	12.8	*i*
(6)	$CHCl_2F$	−50	1.13, 1.14, 1.18, 1.43	6.9	1.18	15.0	0	31	14.1	*g*
(7)	$CHCl_2F$	−85	2.81	17.9			<−100		<8	*g*
(8)	CH_2:CHCl	−100	2.89	13	1.29	21.5	<−140		<7	*g*
(9)	[$^2H_8$]Toluene	<−40	2.32, 2.56	8.0, 18.9	*l*	*l*	−40	*l*	11.3	*h*
	CH_2:CHCl	<−40	2.59, 2.76	8.2, 19.1	*l*	*l*	−40	*l*	11.8	*h*
(10)	CCl_3F	−80	2.25, 2.78	6.7, 19.2			−50	104	10.9	*i*
	CS_2	−84	2.31, 2.86	6.6, 19.3			−54	73	10.8	*j*
(11)	$CHCl_2F$	−100	2.69, 2.86	5.9, 18.0	1.19	14.5	−84	36	9.5	*g*
	CH_2:CHCl	<−85	2.64, 2.81	5.8, 18.1	*l*	*l*	−85	*l*	9.4[m]	*h*

[a] Chemical shift of the methyl hydrogens in the *N*-alkyl group at T. [b] Coupling constant between the isopropyl methyl group and the vicinal methine proton or between the *N*-methyl group and the phosphorus atom. [c] Chemical shift of the *P*-methyl or -t-butyl group. [d] Coupling constant between the *P*-alkyl protons and phosphorus. [e] Temperature in the region of maximum exchange broadening where the rate constant (k) was determined. [f] Free energy barrier at T_C calculated using the Eyring equation. [g] Present work. [h] Ref. 9. [i] Ref. 6. [j] Ref. 2. [l] Not reported. [m] Value is for $\Delta H^{\ddagger}$.

accurate lineshape analysis difficult. Therefore the t-butyl doublet was included in the analysis as two additional (non-exchanging) sites. Rate constants (k) determined in the region of maximum exchange broadening and derived free energies of activation ($\Delta G^{\ddagger}$) for the *NN*-di-isopropylphosphonamidothioic chlorides (1)—(3) are given in Table 1. The *NN*-dimethyl compounds (7) and (8) failed to show any signal splitting at low temperature, and the maximum $\Delta G^{\ddagger}$ values were estimated by assuming that P–N bond rotation

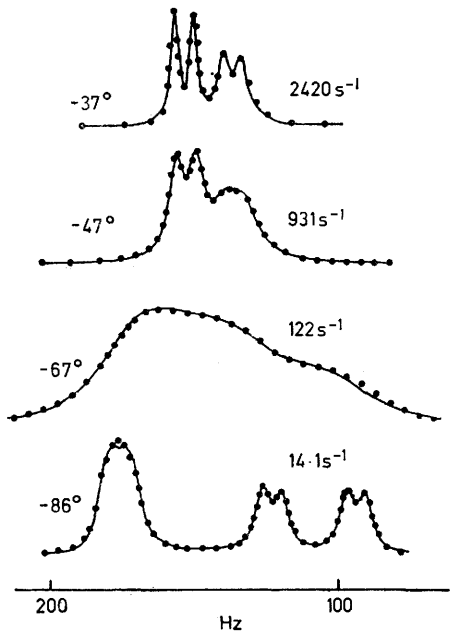
TABLE 2

Enthalpy and entropy of activation for bond rotation in *NN*-di-isopropylphosphonamidothioic chlorides in $CHCl_2F$ solution

Compound	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
(1)	9.6	−1
(2)	8.9	−5
	(8.6)[a]	(−4)[a]

[a] Repeat analysis by another operator using a different sample and a different spectrometer (Varian HA-100).

was fast on the n.m.r. time-scale at the lowest temperature investigated. Rate constants for compounds (1) and (2) in $CHCl_2F$ solution were determined at *ca.* eight temperatures over a range of *ca.* 35°. The enthalpy and entropy of activation are given in Table 2. It is now known that the dynamic n.m.r. method can give rise to large systematic errors in derived enthalpies and entropies of activation. These errors can be enormous where simple approximate methods are used to estimate the exchange rate.[18,19] Even when careful computer assisted lineshape analysis is used,



Experimental (●) and 'best fit' computed (solid line) bandshapes for the isopropyl methyl signals of *NN*-di-isopropyl-*P*-phenylphosphonamidothioic chloride (2) at various temperatures in $CHCl_2F$ solution. The calculated site exchange rates are also shown

the errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are commonly 1—3 kcal mol^{-1} and 5—10 cal K^{-1} mol^{-1} respectively.[20] * The entropy of

* A referee has commented on the possibility that non-Lorentzian lineshapes could give rise to errors in iterative bandshape fitting (this danger is also present in visual fitting). Markedly non-Lorentzian lineshapes can arise from inadequate spectrometer settings (*e.g.* curvature or phase) or from unresolved coupling. It should be emphasised that if the lineshapes in the slow exchange region vary significantly from Lorentzian or if the linewidth is of the comparable magnitude to the signal separation, bandshape analysis should be confined to the region of maximum exchange broadening and derived activation parameters confined to $\Delta G^{\ddagger}$.

[18] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 1966, **88**, 3185.
[19] I. O. Sutherland, *Ann. Reports N.M.R. Spectroscopy*, 1971, **4**, 71.
[20] R. R. Sharp, E. D. Becker, and M. L. McNeal, *J. Phys. Chem.*, 1972, **76**, 71.

activation for an intramolecular process such as bond rotation would normally be expected to be close to zero, except possibly in highly hindered systems or where the transition state has a high degree of dipolar character and the study is conducted in a polar solvent. No particular significance is attached to the $\Delta S^{\ddagger}$ values in Table 2 as they are considered to be close to zero within the limits of the method. In the few cases where the entropy of activation for an intramolecular process has been accurately determined it is generally $<$ *ca.* 5 cal K^{-1} mol^{-1}.[19,21-23] Accordingly it is quite reasonable to compare $\Delta G^{\ddagger}$ values determined at different temperatures, since the error in this parameter is usually <0.2 kcal mol^{-1} where a careful computer assisted analysis is performed in the region of maximum exchange broadening (assuming that the signal separation is considerably greater than the linewidths).

EXPERIMENTAL

Materials.—t-Butylphosphonous dichloride was prepared from t-butylmagnesium chloride and phosphorus trichloride in ether at −45 °C under nitrogen.[24] Methylphosphonous dichloride was supplied by Dr. A. F. Childs of Albright and Wilson Ltd., and phenylphosphonous dichloride was available commercially.

Phosphonamidous chlorides were prepared by the slow addition of the amine (2 mol) in ether to the alkyl- or phenyl-phosphonous dichloride in ether at −78 °C.[6] The reaction was carried out under dry nitrogen, and after the addition was complete the mixture was allowed to assume ambient temperature.* After a few hours the amine hydrochloride was filtered off and the product isolated by distillation *in vacuo*. *NN*-Di-isopropyl-*P*-methylphosphonamidous chloride (4) had b.p. 51° at 2 mmHg, *NN*-di-isopropyl-*P*-phenylphosphonamidous chloride (5) had b.p. 84° at 0.05 mmHg (lit,[6] 88° at 0.05 mmHg), and *NN*-dimethyl-*P*-t-butylphosphonamidous chloride (11) had b.p. 55° at 7 mmHg[25]. These compounds rapidly deteriorated in air and showed rather variable analytical data, hence they were characterised as the sulphides (see below).

NN-*Di-isopropyl*-P-*t-butylphosphonamidous Chloride* (6). —Di-isopropylamine failed to react with t-butylphosphonous dichloride in ether even after prolonged reflux. After several unsuccessful attempts using higher boiling solvents it was found that the following procedure provided the required product. t-Butylphosphonous dichloride (12.7 g) was distilled *in vacuo* into a Carius tube containing di-isopropylamine (25 cm^3). The sealed tube was heated for 84 h at 130 °C and the contents extracted with ether, filtered, and distilled. The crude product (10.8 g, 60%), b.p. 54° at 0.15 mmHg was purified by g.l.c. on Sigum–Celite at 152° (Found: C, 53.8; H, 10.4; Cl, 15.8. $C_{10}H_{23}ClNP$ requires C, 53.7; H, 10.4; Cl, 15.9%).

Phosphonamidothioic Chlorides.—An equimolar mixture of the phosphonamidous chloride and powdered sulphur was heated in boiling benzene under nitrogen for *ca.* 24 h [65 h in the case of compound (8)]. The solution was then filtered and concentrated to give the crude product. The pure phosphonamidothioic chloride was obtained in 30—60% yield after distillation, recrystallisation, or preparative g.l.c. NN-*Di-isopropyl*-P-*methylphosphonamidothioic chloride* (1) had b.p. 82° at 0.1 mmHg, m.p. 45° (Found: C, 39.8; H, 8.2; N, 6.1; Cl, 16.7. $C_7H_{17}ClNPS$ requires C, 39.4; H, 8.0; N, 6.6; Cl, 16.6%). NN-*Di-isopropyl*-P-*phenylphosphonamidothioic chloride* (2) had m.p. 95° (from light petroleum) (Found: C, 52.4; H, 7.0; Cl, 13.1. $C_{12}H_{19}ClNPS$ requires C, 52.2; H, 7.0; Cl, 12.9%). NN-*Di-isopropyl*-P-*t-butylphosphonamidothioic chloride* (3) had m.p. 54° after sublimation *in vacuo* (Found: C, 47.7; H, 9.4; N, 5.5; Cl, 14.0. $C_{10}H_{23}ClNPS$ requires C, 47.0; H, 9.1; N, 5.5; Cl, 13.9%). NN-*Dimethyl*-P-*t-butylphosphonamidothioic chloride* (8), m.p. 96°, was purified by g.l.c. on Sigum–Celite at 151° (Found: C, 36.4; H, 7.6; Cl, 17.4; N, 6.9. $C_6H_{15}ClNPS$ requires C, 36.1; H, 7.6; Cl, 17.7; N, 7.0%). NN-*Dimethyl*-P-*phenylphosphonamidothioic chloride* (7) was prepared by treating phenylphosphonothioic dichloride in ether solution at −78 °C with a two molar proportion of dimethylamine. After refluxing for 4 h the solution was filtered, concentrated, and distilled *in vacuo* to afford the *product*, b.p. 122—113° at 0.2 mmHg (Found: C, 43.5; H, 4.9; Cl, 16.2; N, 6.7. $C_8H_{11}ClNPS$ requires C, 43.7; H, 5.1; Cl, 16.1; N, 6.4%).

Dynamic N.m.r. Studies.—These were mainly carried out at 100 MHz on a Varian XL-100 spectrometer [except for compound (4) which was investigated on a Perkin-Elmer R-12B spectrometer at 60 MHz]. Spectra were recorded under slow sweep conditions with radiofrequency power levels well below saturation. Samples (0.080 g or 0.080 cm^3) were transferred into the n.m.r. tube under nitrogen. The solvent (0.50 cm^3) and a trace of tetramethylsilane were distilled into the sample tube using a vacuum line, and the tube was then degassed and sealed. Probe temperature was measured by the replacement method using a Doric digital temperature indicator equipped with a copper–constantan thermocouple inserted into a tube (at the level of the receiver coil) containing an equal amount of solvent as the original sample. The indicator was frequently checked using the b.p. of water, the m.p. of ice, and the sublimation temperature of carbon dioxide as reference points. Data analyses were carried out on the University English Electric KDF9 or ICL 1906A digital computer. Graphical display of calculated and experimental spectra was obtained *via* a Digital Electronics PDP8 computer controlling a Calcomp graph plotter.

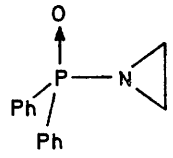
DISCUSSION

Phosphonamidothioic Chlorides.—The two sets of methyl signals (d, $^3J_{HH}$ *ca.* 6.8 Hz) in the proton n.m.r. spectra of compounds (1)—(3) at ambient temperature arise from geminal methyl non-equivalence due to the absence of a molecular symmetry plane through the acyclic prochiral methine carbon atoms.[10] At room temperature the two isopropyl groups are rendered stereochemically equivalent on the n.m.r. time-scale by rapid inversion of the prochiral nitrogen atom combined with fast rotation around the P–N bond (assuming rapid

* It has been previously reported [9] that the reaction between t-butylphosphonous dichloride and dimethylamine was extremely sluggish, even at 100 °C, necessitating the use of lithium dimethylamide. However we found that combination of t-butylphosphonous dichloride and dimethylamine in ether solution at −78 °C followed by standing for 3 h at ambient temperature gave on distillation the phosphonamidous chloride in 60% yield.

[21] A. Jaeschke, H. Muensch, H. G. Schmid, H. Friebolin, and A. Mannschreck, *J. Mol. Spectroscopy*, 1969, **31**, 14.
[22] M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, 1971, **93**, 685.
[23] J. Bjørgo and D. R. Boyd, *J.C.S. Perkin II*, 1973, 1575.
[24] W. Voskuil and J. F. Arens, *Rec. Trav. chim.*, 1963, **82**, 302.
[25] S. Chan, S. DiStefano, F. Fong, H. Goldwhite, P. Gysegem, and E. Mazzola, *Synthesis Inorg. Metal-org. Chem.*, 1972, **2**, 13.

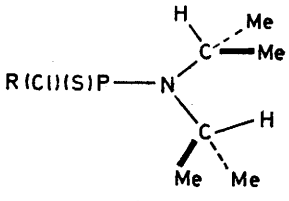
rotation around the *N*-isopropyl bonds). However, the observation of four methyl doublets at low temperature indicates that the isopropyl groups have become non-equivalent. This was confirmed by carbon-13 spectra at −90° which show two methine carbon signals and four methyl signals.[26] On warming to ambient temperature the methine carbon signals had coalesced to a single signal and the four methyl ^{13}C resonances had coalesced to two. The observation of diastereotopic isopropyl groups in the ^{1}H and ^{13}C spectra at low temperatures indicates that either nitrogen inversion or P–N bond rotation had become slow on the n.m.r. time-scale. It is now fairly well established that aminophosphorus compounds have very low barriers to pyramidal inversion at nitrogen.[6] Thus the nitrogen inversion barrier in aziridin-1-yl(diphenyl)phosphine oxide[27] (12) is 8.2 kcal mol^{-1} compared with 19.4 and 17.0 kcal mol^{-1} in *N*-methyl-[28] and *N*-butyl-aziridine[29] respectively. Acyclic



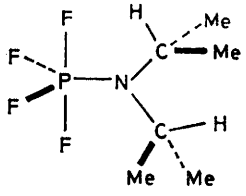
(12)

amines have inversion barriers of *ca.* 6 kcal mol^{-1},[28,30] and the presence of an adjacent phosphorus atom should facilitate the inversion process. Indeed, the inversion barrier in an acyclic dialkylamino(diphenyl)phosphine oxide may be estimated to be only *ca.* 3 kcal mol^{-1} from the linear free energy relationship proposed by Splitter and Calvin.[31] It is probable that the presence of an electron-withdrawing chlorine substituent on phosphorus would further reduce the nitrogen inversion barrier by enhancing the π-acceptor tendency of the phosphorus group. Indeed, the nitrogen atom in difluoro(dimethylamino)phosphine is planar in the solid state.[32] Accordingly, it would seem that the barriers reported in Tables 1 and 2 can be confidently assigned to P–N bond rotation. However, there is another way that isopropyl group non-equivalence might be achieved without invoking slow P–N bond rotation. Thus if rotation around the *N*-isopropyl bonds were slow on the n.m.r. time-scale the molecule could become frozen into conformation (13).

Although this suggestion might seem unlikely, there is a recent precedent for such a ' cogwheel ' arrangement of *N*-di-isopropyl groups in an aminophosphorus compound. Cowley *et al.*[33] have carried out a detailed ^{1}H, ^{19}F, ^{31}P,



(13)



(14)

and ^{13}C n.m.r. investigation of di-isopropylaminotetrafluorophosphorane and concluded that the di-isopropylamino-group is frozen into the arrangement (14) below −60°. A similar ' cogwheel ' arrangement has previously been postulated to account for the non-equivalence of *N*-isopropyl signals in the low temperature spectra of *NN*-di-isopropyl-thioamides and -dithiocarbamates.[34-36] The observation that the dimethylamino-compounds (7) and (8) do not show anisochronous *N*-methyl signals at low temperature (Table 1) might be cited in support of the view that the spectral changes in the corresponding di-isopropyl compounds could be due to slow rotation around the *N*-isopropyl bonds. However, it is known from previous investigations of aminophosphorus and -sulphur compounds that the barrier to rotation around the P–N or S–N bond is considerably enhanced on increasing the bulk of the *N*-alkyl substituents.[6,7,9,37,38] It can be seen from the data for compounds (1)—(3) (Table 1) that the free energy of activation is increased by 2.5 kcal mol^{-1} on increasing the size of the *P*-alkyl substituent from methyl or phenyl to t-butyl. This steric effect at phosphorus is more readily rationalised in terms of rotation around the P–N bond rather than the more remote C–N bonds.

It has been proposed that directional π-bonding in P–N and S–N bonds may contribute to the enhanced torsional barriers found in some aminophosphines and aminosulphur compounds bearing an electron-withdrawing substituent on the phosphorus or sulphur atoms.[1-8,37,38] This π-bonding was originally considered to be of the $(p–d)_\pi$ type arising mainly from overlap of the filled lone pair orbital on nitrogen with vacant *d*-orbitals on the second-row element. Alternatively it has been suggested for aminosulphur compounds that directional π-bonding in the N–S bond may arise from overlap of the nitrogen lone pair with an antibonding *sp* hybrid orbital on sulphur which is *anti* to the electronegative sulphur substituent.[39] An $n–\sigma^*$ bond of this type [see (15)]

[26] J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *Tetrahedron Letters*, 1973, 4919.
[27] F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357.
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[31] J. S. Splitter and M. Calvin, *Tetrahedron Letters*, 1973, 4111.
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[33] A. H. Cowley, R. W. Braun, and J. W. Gilje, *J. Amer. Chem. Soc.*, 1975, **97**, 434.
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[35] C. Roussel, M. Chanon, and J. Metzger, *Tetrahedron Letters*, 1971, 1861; 1972, 3843.
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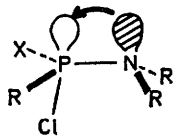
[37] M. Raban, G. W. J. Kenney, and F. B. Jones, *J. Amer. Chem. Soc.*, 1969, **91**, 6677; M. Raban and F. B. Jones, *ibid.*, 1971, **93**, 2692.
[38] W. R. Jackson, T. G. Kee, and W. B. Jennings, *J.C.S. Chem. Comm.*, 1972, 1154; W. B. Jennings and R. Spratt, *ibid.*, 1970, 1418.
[39] M. Raban and D. Kost, *J. Amer. Chem. Soc.*, 1972, **94**, 3234; see also G. Braddeley, *Tetrahedron Letters*, 1973, 1645.

might also be proposed as an alternative to $(p–d)_\pi$ bonding in aminophosphorus compounds. Indeed, recent *ab initio* MO calculations on $PH_2–NH_2$ suggest that the phosphorus *d*-orbitals do not play a significant role in the bonding.[40] However, there is no evidence that the P–N torsional barriers in the phosphonamidothioic chlorides (Table 1) are any larger than could be accounted for in



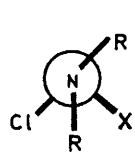
(15)

terms of normal steric interactions between vicinal substituents. Clearly there is no *large* contribution to the PN torsional barrier in these compounds from directional π-bonding.

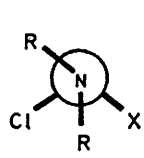
Phosphonamidous Chlorides.—Data for P–N bond rotation in the corresponding phosphorus(III) compounds (4)—(6) and (9)—(11) are also given in Table 1. Several of these compounds have been previously investigated by dynamic n.m.r., but when this study was initiated no data were available for compounds (4), (6), and (11). Recently, Goldwhite and his co-workers [9] have independently measured the P–N rotational barriers in compounds (4) and (6) and their data are also included in Table 1.

The barriers in the phosphonamidous compounds are generally 2—3 kcal mol^{-1} higher than in the corresponding phosphonamidothioic compounds. This would be consistent with the phosphorus lone pair in the phosphonamidous chlorides being associated with the enhanced rotational barriers, though whether the effect is mainly due to repulsion between vicinal lone pairs is open to speculation.[6] However, it is also possible that trivalent phosphorus is a better acceptor for the nitrogen lone pair electrons in *p–d* or *n*–σ* π-bonding.

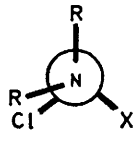
It has previously been observed that P–N rotational barriers increase with the steric bulk of the *N*-alkyl substituents,[6,7,9] and this effect is clearly reflected in the higher barriers for the *N*-isopropyl compounds (4)—(6) as compared with the *N*-methyl analogues (9)—(11). One would expect the *P*-alkyl substituent to exert a similar effect on the P–N rotational barrier. However in the *NN*-dimethyl-*P*-alkylphosphonamidous chlorides the P–N rotational barrier is reduced by *ca.* 2 kcal mol^{-1} (Table 1) on changing the phosphorus substituent from methyl (9) or phenyl (10) to t-butyl (11). Similar observations have been reported independently by Goldwhite *et al.*[9] However, this inverse steric effect of the *P*-alkyl group is not observed in the corresponding diisopropylamino-compounds where the barrier in the *P*-t-butyl compound (6) is slightly higher than in the *P*-methyl and -phenyl compounds (4) and (5). The phosphonamidothioic compounds also show normal *P*- and *N*-alkyl steric effects on the rotational barrier. The reason for the anomalous *P*-alkyl substituent effect in compound (11) is not readily apparent, though it would suggest that the ground state is more hindered than the transition state for the rotation–inversion process. In this connection it may be relevant that the preferred ground-state conformation of aminophosphorus(III) compounds has the vicinal lone pair electrons approximately gauche (16) or (17).[6]



(16)



(17)



(18)

Neither of these conformations may minimise the steric interactions between the substituents on nitrogen and phosphorus. Of the two gauche conformers (16) and (17) the latter might be predicted to be more favourable since it places the phosphorus lone pair electrons *anti* to the electronegative chlorine substituent and suffers less steric interactions than (16). Rotation around the P–N bond in compound (11), where R = Me and X = Bu^t, may occur *via* conformation (18) which eclipses only two substituents (Cl and *N*-methyl). This process could be accelerated by a complete removal of the Bu^t–*N*-alkyl interaction present in (17). This suggestion would also be consistent with the normal steric effects observed for *N*-alkyl substituents since rotation from conformation (17) through (18) enhances the steric interaction between the chlorine atom and the proximate *N*-alkyl group. It still remains to explain why the barrier in the *N*-diisopropyl-*P*-t-butyl compound (6) is not lowered relative to the *P*-methyl compound (4). Possibly this compound is so hindered that the ground state conformation is no longer gauche.

Carbon–Phosphorus Bond Rotation.—Two groups of investigators [41,42] have independently reported that t-butyldichlorophosphine, Bu^tPCl_2, exhibits slow rotation (on the n.m.r. time scale) around the carbon–phosphorus bond at *ca.* −150° as revealed by non-equivalent t-butyl methyl groups. It would be of interest to have C–P rotational barriers for the t-butyl compounds in Table 1 to compare with the P–N barriers.

NN-Di-isopropyl-*P*-t-butylphosphonamidothioic chloride (3) and the corresponding *NN*-dimethyl compound (8) were investigated down to −150 and −158° respectively in vinyl chloride solution, but although the t-butyl doublet ($^3J_{PH}$ 21.5 Hz) had collapsed to a very broad signal at the lowest temperature attained, no signal splitting was evident. Similarly the corresponding phosphonamidous compounds (6) and (11) only showed considerable broadening of the t-butyl doublet ($^3J_{PH}$ 15 Hz) down to −130° in $CHCl_2F$ solution.

[40] I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *J.C.S. Chem. Comm.*, 1974, 432.

[41] J. B. Robert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1972, **94**, 4902.

[42] C. H. Bushweller and J. A. Brunelle, *J. Amer. Chem. Soc.*, 1973, **95**, 5949.

Accordingly, the carbon–phosphorus rotational barrier in these compounds is probably somewhat lower than the 6 kcal mol^{-1} observed in t-butyldichlorophosphine. The carbon–phosphorus barriers in these compounds are clearly much lower than the phosphorus–nitrogen barriers in the phosphonamidous compounds. These observations lend further support to the view that the latter barriers are anomalously high due to vicinal lone pair repulsion and/or π-bonding in the P–N bond.

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