perience greater deshielding effects from proximal aniso-
tropic pyridine molecules coordinated to the OH proton.

Subtle conformational differences in ring C between
compound **2** and compounds **3** and **5** are indicated from
the solvent shift results recorded for the C_{10} methylene
protons (see Table I). Thus, in **2**, relative to **3** and **5**,
both the C_{10} protons resonate to low enough field (in
C_5D_5N) to be readily identifiable and, in addition, both
$H_{10\beta}$ axial and $H_{10\alpha}$ equatorial experience smaller (but
similar) solvent deshielding effects ($\Delta = -0.44$ and
-0.35 ppm, respectively) than corresponding protons
in **3** and **5**. Since the magnitude of pyridine solvent
shifts is distance dependent,[16] these results are in cor-
roboration with the conclusions of the previous section
in that, in **2**, ring B assumes the other possible confor-
mation such that the C_{10} methylene protons are almost
equidistant from the phenolic oxygen. This is in con-
trast to the conformation of ring B of compounds **3**
and **5** where $H_{10\alpha}$ equatorial is considerably closer
to the phenolic OH (and hence the large solvent
shift) than $H_{10\beta}$ axial. These conclusions are in good
accord with the internuclear distance, r, between the
phenolic oxygen and C_{10} protons obtained from the
Westheimer method. Thus, in **1** ($r_{H_{10}-O_1} = 2.30$ Å)
and **3** ($r_{H_{10\alpha}-O_1} = 2.34$ Å and $r_{10\beta-O_1} = 3.46$ Å), H_{10}
and $H_{10\alpha}$ are in close proximity to the phenolic oxygen,
whereas in **2** ($r_{H_{10\alpha}-O_1} = 2.65$ Å and $r_{H_{10\beta}-O_1} = 2.48$ Å),
$H_{10\alpha}$ and $H_{10\beta}$ are located at nearly equal but intermedi-
ate distances from the phenolic oxygen.

Experimental Section

$l\text{-}\Delta^9\text{-}THC$ (**1**) and $l\text{-}\Delta^8\text{-}THC$ (**5**) were obtained from R. Mechou-
lam, Laboratory of Natural Products, School of Pharmacy, The
Hebrew University, Jerusalem, Israel. Gas–liquid partition chro-
matography (glpc)[34] indicated that the purity of these samples was
about 95%. The 3-n-hexyl analog of $\Delta^{6a(10a)}\text{-}THC$ (**2**) ("synhexyl")
was obtained from Abbott Laboratories. Glpc indicated that the
sample was at least 90% pure. $l\text{-}trans\text{-}$Hexahydrocannabinol (**3**)[4c]
was prepared by taking a 313-mg sample of $\Delta^8\text{-}THC$ (**5**) in 35 ml
of ethanol and hydrogenating over 50 mg of PtO_2 for 4 hr at 45 psi
pressure. Evaporation of the solvent after removal of the catalyst
by suction filtration gave 300 mg of a light tan resin. Glpc and
tlc investigation indicated that the product was a mixture of two
isomers. The molecular weight of HHC (**3**) was confirmed by
high-resolution mass spectrometry.

Nmr spectra were recorded using a Varian HR-220 spectrometer.
Decoupling and NOE studies were carried out on a Varian HA-100
spectrometer in the frequency sweep mode. NOE effects were
measured on nitrogen-sparged solutions (sample concentrations
were approximately 8% w/v) with TMS as internal lock and refer-
ence. The irradiating audiooscillator was a Hewlett-Packard 200
ABR, and power requirements for NOE studies were determined by
slowly increasing millivolt output until area increases were opti-
mized. Each peak indicating increases in signal height was integrated
at least ten times with and without optimum power and NOE's
calculated from the average values.

The Stereochemistry of Aminophosphines[1]

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Abstract: The proton magnetic resonance (pmr) spectra of a series of aminophosphines, R_2NPXY, have been
examined over the temperature range 40 to $-150°$. In the majority of these compounds the nitrogen substituents,
R, became diastereotopic at low temperatures. Using the technique of matching the observed and computer simu-
lated line shapes, it was possible to calculate the rates of, and activation parameters for, the implied stereochemical
changes. The observed steric deceleration with increasing steric bulk of the nitrogen substituents, together with
the inability to observe a barrier in 2,2-dimethyl-1-diphenylphosphinoaziridine, provide evidence that the observed
barriers in the acyclic aminophosphines relate to torsion around the phosphorus–nitrogen bond rather than to
pyramidal nitrogen inversion. The origins of these barriers are discussed from the standpoints of steric effects, lone
pair–lone pair repulsions, and $p\pi$–$d\pi$ bonding. In contrast to an earlier report it is found that the symmetrical
aminophosphines, R_2NPX_2, are still undergoing rapid P–N bond rotation on the nmr time scale at $-80°$. The ob-
servation of diastereotopic R groups below $-120°$, together with steric considerations, suggests that the *gauche*-type
conformation is adopted at low temperatures. The pmr spectra of $C_6H_5As(Cl)N(CH_3)_2$ have also been recorded
over a wide range of temperatures, leading to the measurement of the first arsenic–nitrogen rotational barrier.

There is considerable current interest in the use
of nuclear magnetic resonance (nmr) to investigate
the stereochemistry of trivalent nitrogen attached to
group V and group VI heteroatoms. This area en-
compasses hydrazines,[4] aminophosphines,[5–8] hydroxyl-

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amines,[9] sulfinamides,[10] and sulfenamides.[11,12] The principal points of interest in these studies have centered around the identification of the rate-determining stereochemical processes, assessment of the conformational preferences at low temperatures, and evaluation of the various factors which might influence the magnitudes of the rotational or inversional barriers. In the case of the aminophosphines the phosphorus and nitrogen atoms each possess a lone pair of electrons; hence the possible stereochemical processes comprise rotation around the phosphorus–nitrogen bond, and pyramidal inversions at both nitrogen and phosphorus. However, phosphorus inversion is a relatively high energy process (see later) which is not expected to occur in the temperature range of concern here. The choice between P–N torsion and pyramidal nitrogen inversion as the rate-determining step is not trivial because barriers to nitrogen inversion can vary over a wide range. Thus, in some cases it has been shown[4d,f,13,14] that the presence of a heteroatom directly bonded to nitrogen substantially raises this barrier, while in others, where the possibility of a $p\pi$–$d\pi$ interaction exists, the barrier is reduced.[12,15] In our preliminary communication[6] it was argued that P–N bond torsion was the rate-controlling feature in acyclic aminophosphines. In the present paper these arguments are strengthened by data for more compounds and by failure to detect a nitrogen inversional barrier in 2,2-dimethyl-1-diphenylphosphinoaziridine down to $-150°$. By extending the measurements to temperatures below $-100°$, it has also become possible to measure the P–N rotational barriers in symmetrically substituted aminophosphines of the type $(CH_3)_2NPX_2$. The spectral observations on these compounds are important because they provide new evidence concerning the conformational preference of aminophosphines at low temperature. Another concern of the present paper is an attempt to assess the relative importance of steric effects, lone pair–lone pair repulsions, and $p\pi$–$d\pi$ bonding in maintaining the preferred geometry. Finally, proton nmr spectral data are presented for the aminoarsine, $C_6H_5As(Cl)N(CH_3)_2$, leading to the measurement of the first arsenic–nitrogen rotational barrier.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories. All melting point samples were sealed in capillaries under an argon atmosphere. All operations involving the aminophosphines were carried out either under an inert atmosphere or by standard vacuum line techniques.

Materials. 2,2-Dimethylaziridine, bp 69–70° (760 mm), was prepared by the method of Cairns.[16] Methylamine-N-d_2 was prepared by the exchange of CH_3NH_2 with D_2O.[17] The exchange reaction was allowed to proceed until the deuterium content of the amine was greater than 90% on the basis of nmr and mass spectroscopy. The chlorophosphines CF_3PCl_2 and $(CF_3)_2PCl$ were obtained from the reaction of the corresponding iodophosphines with $HgCl_2$.[18] The other starting materials were procured commercially and used without further purification. Trichlorofluoromethane ("Freon-11") and dichlorofluoromethane ("Genetron-21") were obtained from Matheson and had purities of 99.9 and 99.0%, respectively.

The following aminophosphines were prepared by slow addition of the appropriate quantity of the amine in ether solution to a stirred ethereal solution of the halophosphine at a temperature below $-10°$.[19] The stirred solution was allowed to assume ambient temperature and stirring was maintained for a few hours thereafter. The amine hydrochloride was then filtered off, the solvent stripped off under reduced pressure, and the crude product purified by fractional vacuum distillation

Chloro(dimethylamino)phenylphosphine, bp 47–50° (0.25 mm) (lit.[20] bp 79° (2.5 mm)).

Dimethylamino(diphenyl)phosphine, mp 32–33°; bp 96.7° (0.015 mm) (lit.[21] mp 31.5–33.5°; bp 123–124° (0.1 mm)).

Dichloro(dimethylamino)phosphine, bp 57–59° (24 mm) (lit.[22] bp 150° (760 mm)).

Chloro(diethylamino)phenylphosphine, bp 146–148° (2 mm) (lit.[23] bp 82–84° (0.05 mm)).

Diethylamino(diphenyl)phosphine, bp 125–127° (0.07 mm) (lit.[23] bp 126° (0.1 mm)).

Dichloro(dimethylamino)phosphine, bp 75–78° (22 mm) (lit.[22] bp 78° (17 mm)).

Chloro(dibenzylamino)phenylphosphine, bp 170–175° (0.05 mm), mp 47–49°. *Anal.* Calcd for $C_{20}H_{19}ClNP$: C, 70.7; H, 5.6; Cl, 10.4; N, 4.1; P, 9.1. Found: C, 70.4; H, 5.65; Cl, 10.0; N, 4.0; P, 9.5.

Chloro(diisopropylamino)phenylphosphine, bp 87–88° (0.05 mm) (lit.[7] bp 122° (0.2 mm)). *Anal.* Calcd for $C_{12}H_{19}ClNP$: C, 59.1; H, 7.8; Cl, 14.85; N, 5.7; P, 12.7. Found: C, 59.0; H, 7.8; Cl, 14.6; N, 5.6; P, 12.6.

Chlorobis(dimethylamino)phosphine, bp 68° (11 mm) (lit.[20] bp 64° (10 mm)).

2,2-Dimethyl-1-diphenylphosphinoaziridine, bp 120–124° (0.2 mm), mp 48–50°. *Anal.* Calcd for $C_{16}H_{18}NP$: C, 75.3; H, 7.1; N, 5.5. Found: C, 75.2; H, 7.2; N, 5.3.

Chloro(dimethylamino)phenylarsine, bp 49–50° (0.05 mm). *Anal.* Calcd for $C_8H_{11}AsClN$: C, 41.5; H, 4.8; Cl, 15.3. Found: C, 41.65; H, 4.9; Cl, 15.2.

The volatile aminophosphines $(CH_3)_2NP(Cl)CF_3$,[24] $(CH_3)_2NP(CF_3)_2$,[25] and $CH_3N(H)P(CF_3)_2$[25] were prepared by published procedures and fractionated by trap-to-trap distillation until their vapor pressures conformed to the literature values. The N-deuterio compound, $CH_3N(D)P(CF_3)_2$ was prepared by a modification of Harris' method[25] in which CH_3NH_2 was replaced by CH_3ND_2. The vapor pressure was 26.4 mm at 0°.

Nmr Spectra. All spectra were determined on a Varian Associates HA-100 spectrometer equipped with a variable-temperature accessory. Probe temperatures down to $-60°$ were calibrated against methanol spectra as described in the Varian Users Manual. Temperatures below $-60°$ were measured by inserting a copper-constantan thermocouple into a sample tube containing 0.5 ml of a mixed isohexanes solution. The thermocouple was calibrated before each experiment using the boiling point of water and the sub-

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Table I. P–N Bond Rotational Barriers and Spectral Data for Chloro(dialkylamino)phenylphosphines, $C_6H_5P(Cl)NR_2$

R	Solvent	Temp, °C	τ_{CH_3}[a]	J_{PNCH}, Hz	Other couplings, Hz	T_{coales}, °C	Exchange rate,[b] sec⁻¹	$\Delta F^\ddagger$,[c] kcal/mol⁻¹
CH_3	$CFCl_3$	30	7.40	12.6				
		−80	7.22	19.2		−50	104	10.9
			7.75	6.7				
CH_2CH_3	$CFCl_3$–$CDCl_3$ (1:1)	30	8.92 t	12.0	$J_{HCH} = 7.1$	−57	50	10.8
		−80	8.74 t, 9.05 t					
$CH_2C_6H_5$	$CDCl_3$	30	5.91 q[d]	e	$J_{HCH} = 14.4$	−46		f
		−70	5.72 q, 6.28 q[d]	e	$J_{HCH} = 15.8$			
$CH(CH_3)_2$	$CFCl_3$	30	8.71 d, 8.91 d	10.0	$J_{PNCH} = \sim 0.5$	−15	70	12.8
		−50	8.55 d, 8.63 d,		$J_{HCCH} = 6.7$	(−10)[h]	105	12.9
			8.89 d, 9.17 d			(−5)[h]	250	12.7
$CH(CH_3)CH_2CH_3$[g]	CS_2		8.7			15		14.6[g]

[a] d = doublet; t = triplet; q = AB quartet. [b] Exchange rates were calculated at the coalescence temperature using a computer simulated line shape analysis procedure; the program was of the many site type (see text). [c] Derived from the Eyring equation assuming a transmission coefficient of unity. [d] Methylene proton absorptions. [e] Spectra were observed with irradiation at the ^{31}P frequency. [f] Not determined owing to the complexity of the spectra. [g] Values taken from ref 7. [h] Additional temperature at which the exchange rate was determined.

Table II. P–N Bond Rotational Barriers and Spectral Data for Aminophosphines, R_2NPXY

R	X	Y	Solvent	Temp, °C	τ_{CH_3}	J_{PNCH}, Hz	Other couplings, Hz	T_{coales}, °C	Exchange rate, sec⁻¹	$\Delta F^\ddagger$,[a] kcal/mol
CH_3	Cl	Cl	$CHFCl_2$	−74	7.12	12.4		−113	14[c]	8.4
				−125	7.06	19.2		(−107)[b]	35[c]	8.3
					7.10	4.9				
CH_3	CF_3	CF_3	CF_2Cl_2	−80	7.07	8.9	J_{FCNPCH} 0.5	−105[d]	15[d]	8.7
				−142	7.03	∼14		(−107)[b,d]	8.5[d]	8.8
					7.10	∼4		(−96)[b]	40[c]	8.9
CH_3	Cl	CF_3	$CFCl_3$	30	7.07	11.2	J_{FCPNCH} 0.5	−70	34	10.5
				−100	6.98	18.1		−75[d]	∼30	∼10.2
					7.11	5.0				
CH_3	C_6H_5	C_6H_5	$CHFCl_2$	−130	7.48	9.8		<−130[e]		
CH_3	F	F	$CHFCl_2$	−108	7.25	9	J_{FPNCH} 4	<−120[e]		
CH_2CH_3	C_6H_5	C_6H_5	$CHFCl_2$	−80	9.08	9.5	J_{HCCH} 7.0	<−120[e]		
CH_2CH_3	Cl	Cl	$CFCl_3$–$CDCl_3$ (1:1)	−80	8.81	13.0	J_{HCCH} 7.2	<−80		
CH_3	Cl	$N(CH_3)_2$	$CHFCl_2$	−120	7.26	12.3		<−140		

[a] The free energy of activation was calculated from the Eyring equation assuming a transmission coefficient of unity. [b] Additional temperature at which the exchange rate was determined. [c] Exchange rate was determined by comparison with spectra computed for exchange between four sites (see text). [d] Spectra observed with irradiation at the ^{31}P frequency; the exchange rate was determined by comparison with spectra computed for a simple two site exchanging system. [e] Below this temperature the signals became very broad, but no additional splitting was observed down to −140°.

limation temperature of carbon dioxide as reference points.[26] Spectra which involved saturation at the ^{31}P frequency were performed using an NMR Specialties HD-60B decoupler.

The volatile aminophosphines were distilled into the nmr tubes on the vacuum line, and the less volatile compounds were transferred under an inert atmosphere. The appropriate solvent was then distilled in using the vacuum line, together with a few per cent of tetramethylsilane (TMS) as internal standard. The samples were then degassed several times by the freeze-thaw method and sealed *in vacuo* at −196°.

Line-Shape Calculations. Theoretical spectra were calculated using the University of Texas CDC 6600 digital computer, and plotted on microfilm. For exchange processes involving more than two sites, the spectra were calculated using a many site program NMRLS, based on the equations of Anderson and Kubo.[27] The program was devised by Professor M. Saunders[28] and modified for the CDC 6600. Input included the frequencies of the lines mea-

sured from an arbitrary zero, their natural line widths and relative intensities in the absence of exchange, and the first-order rate constants for transitions from the ith to the jth sites.

Spectra for chloro(dimethylamino)phenylphosphine and chloro-(dimethylamino)trifluoromethylphosphine, which were observed with phosphorus decoupling, involved exchange between two sites. Theoretical spectra were generated using a program[29] based on the theory of Gutowsky and Holm.[30] In the case of dimethylamino-bis(trifluoromethyl)phosphine (observed with ^{31}P decoupling) and chloro(dimethylamino)phenylarsine, the exchange rates were computed using a program CURVEG which iterated the exchange rate to give the best least-squares fit to the digitized experimental spectrum. The main program was supplied by Professor H. S. Gutowsky,[31] and the line shape for two site exchange was generated using a subroutine SPECG based on the complete line-shape function of Gutowsky and Holm.[30]

Results

The exchange rates in the region of coalescence were calculated by the complete line-shape method, and the results are presented in Tables I and II. The

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spectra of the dimethylaminophosphines at low temperatures consisted of four lines which are attributed to coupling of each of the diastereotopic[32] methyl groups to the phosphorus atom (J_{PNCH} = 4–20 Hz). At higher temperatures the four lines collapsed to a doublet, the separation of which corresponded to a mean J_{PNCH}. The computed spectra in these cases were generated using a many site exchange program (see Experimental Section), by treating the phosphorus coupling as producing additional sites. The nature of the exchange process leading to collapse is controlled by the transition probabilities between the various sites.[28] For example, in the case of chloro(dimethylamino)phenylphosphine, where the chemical shift nonequivalence of the methyl groups is greater than either J_{PNCH},[6] the transition probabilities ($P_{i,j}$) for transition from the ith to the jth site are: $P_{1,2}$ = $P_{1,4}$ = $P_{2,3}$ = $P_{3,4}$ = $P_{2,1}$ = $P_{4,1}$ = $P_{3,2}$ = $P_{4,3}$ = 0, and $P_{1,3}$ = $P_{2,4}$ = $P_{3,1}$ = $P_{4,2}$ = 1, where the four lines in the low-temperature spectrum are numbered from low field to high field.

The spectra of chloro(diisopropylamino)phenylphosphine were further complicated by the chiral center[32] at phosphorus which makes the methyl groups (within each isopropyl moiety) diastereotopic even when rotation around the PN bond is rapid on the nmr time scale, as is the case at ambient temperature (Figure 1). The unequal intensities of the methyl doublets at 30° are due to residual exchange broadening which is greater for the doublet at high field. At −50°, slow PN rotation makes the isopropyl groups nonequivalent, and this, together with the nonequivalence within each isopropyl group, accounts for the four different methyl signals observed at −50° (Figure 1). The eight-line spectrum arises from coupling of each of the four anisochronous methyl groups to the methine proton. The chemical shifts and coupling constants were found to be essentially unchanged at −80°. Spectra under exchanging conditions were calculated for the collapse of eight lines to four lines, assuming the HCCH coupling to be first order. The appropriate "probability matrix"[28] was constructed to reproduce the observed spectra in the limit of fast exchange. Numbering the lines in the −50° spectrum (Figure 1) from left to right (lines 2 and 3 are overlapping), all transition probabilities ($P_{i,j}$) for transitions from the ith to the jth site were taken to be zero except for $P_{1,5}$, $P_{2,6}$, $P_{3,7}$, $P_{4,8}$, $P_{5,1}$, $P_{6,2}$, $P_{7,3}$, and $P_{8,4}$, which were set equal to unity.

The low-temperature spectra for chloro(diethylamino)phenylphosphine contained two triplets which are attributed to the nonequivalent methyl groups. On raising the temperature the pair of triplets collapsed to a single triplet at the mean position. The line shape at coalescence was calculated by treating the individual lines of each triplet as separate sites with the appropriate relative intensities. Although the application of a program based on the Bloch equations must be regarded as approximate in a case such as this, the error should be small since the coupling is close to first order.

The free energies of activation presented in Tables I and II should approximate closely the enthalpies
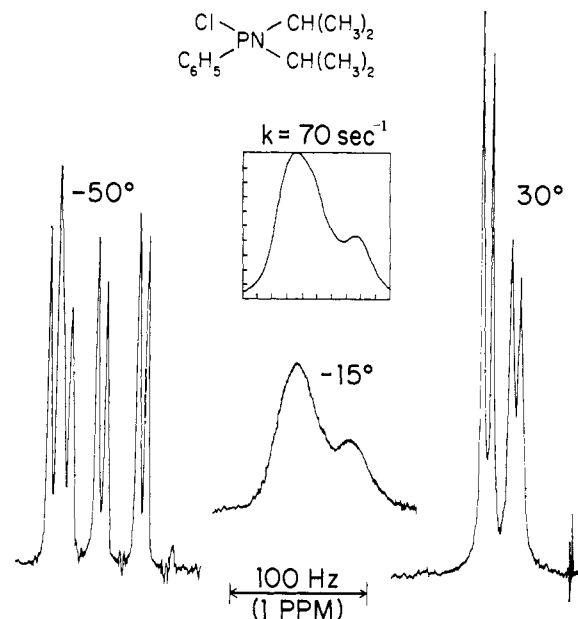

Figure 1. 100-MHz proton nmr spectra of chloro(diisopropylamino)phenylphosphine at various temperatures. The insert is the computer-simulated spectrum in the region of collapse (k = 70 sec^{-1}).

of activation since the entropy of activation of a torsional process of the type considered here should be small. To check this assumption, the exchange rates for chloro(dimethylamino)phenylphosphine were determined at a series of temperatures (in $CFCl_3$ solution) by visual comparison of ^{31}P irradiated spectra with spectra calculated for two-site collapse. The resulting k values (sec^{-1}) are shown in parentheses for the given T (°K) as follows: 238 (555), 233 (294), 228 (200), 223, (117), 218 (59), 215 (50), 213 (35). The best straight line in an Arrhenius plot gave $\Delta E^\dagger$ = 10.9 kcal/mol; $\Delta H^\dagger$ = 11.3 kcal/mol; $\Delta S^\dagger$ = +3 eu. $\Delta F^\dagger$ = 10.8 kcal/mol at the coalescence temperature of −50°. This value for $\Delta S^\dagger$ does not differ from zero by more than the limits of experimental error.

The spectrum of the aminoarsine, $C_6H_5As(Cl)N(CH_3)_2$, consisted of a singlet in the methyl region. Upon cooling, the spectrum collapsed at −100° and at −120° separated into a pair of equally intense lines 41.4 Hz apart (at 100 MHz, in $CHFCl_2$ solution). The signal separation remained essentially unchanged on further cooling, but both signals became very broad and of unequal height. At −135° the signals were so broad that they were barely distinguishable from the noise level. The large broadening effect cannot be ascribed to the viscosity of the solution since the reference signals remained reasonably sharp, nor can it be due to coupling to the arsenic nucleus since quadrapolar relaxation should become faster at lower temperatures.[33] Broadening effects of a comparable magnitude were observed in the low-temperature spectra of $(C_6H_5)_2PN(CH_3)_2$ and $(C_6H_5)_2PN(C_2H_5)_2$, and also in the spectra of hydrazines.[4f,g] It may be that other motions within the molecule are becoming slow below −100°, leading to facile relaxation of the protons. It is interesting in this connection that the broadening effect is largest when bulky phenyl groups

(32) For a discussion of the appropriate nomenclature, see K. Mislow and M. Raban, *Topics Stereochem.*, **1**, 23 (1967).

(33) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958); R. M. Moriarty, J. P. Kim, S. J. Druck, and E. Lustig, *Tetrahedron*, **25**, 1261 (1969).

are present in the molecule. This effect caused difficulties in the calculation of activation parameters by the line-shape simulation procedure. In particular it was necessary to employ a rather wide natural line width (e.g., 8 Hz at $-108°$) to obtain a satisfactory fit to the experimental spectra at and below coalescence. Above the coalescence temperature the signal shape approached Lorentzian; the fit was then no longer sensitive to the natural line width employed, and all that could be done was to employ a line width based on that of the solvent. The resulting k values (sec^{-1}) are shown in parentheses for the given T (°K) as follows: 199 (1312), 194 (860), 189 (480), 184 (348), 178 (200), 173 (120), 166 (84), 165 (70), 159 (43). The best straight line in an Arrhenius plot gave $\Delta E^\dagger = 5.3$ kcal/mol; log $A = 8.9$ sec^{-1}; $\Delta H^\dagger = 5.0$ kcal/mol; $\Delta S^\dagger = 19$ eu. $\Delta F^\dagger = 8.1$ kcal/mol at the coalescence temperature of $-107°$. Similar spectra were observed in CCl$_3$F solution where $\Delta F^\dagger = 8.5$ kcal/mol at the coalescence temperature of $-100°$. The large value of $\Delta S^\dagger$ is probably due to the lower accuracy of these measurements, since $\Delta S^\dagger$ should be approximately zero for such an intramolecular process.

Discussion

(a) The Rate-Determining Stereochemical Process.
The conformational changes which are possible in aminophosphines involve (a) phosphorus pyramidal inversion, (b) nitrogen pyramidal inversion, and (c) rotation around the phosphorus–nitrogen bond. The appropriate transition states for processes a, b, and c are depicted in **1, 2,** and **3.** Of these, phosphorus
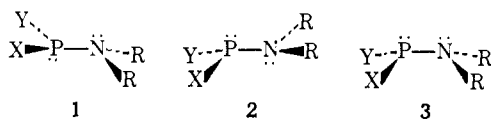
pyramidal inversion can be excluded as a contributor to our observations on energetic grounds. Tables I and II show that the free energies of activation for degenerate racemization of aminophosphines fall in the range 8–12 kcal/mol, much less than the free energy of activation for phosphorus pyramidal inversion in diphosphines[34] ($\sim$26 kcal/mol). In simple tertiary phosphines, the work of Horner and Winkler[35] indicates that the inversional barrier is $\sim$30 kcal/mol and thus outside the range of the nmr method at normal temperatures. Cases of more facile stereomutation at trivalent phosphorus have been shown to involve an intermolecular exchange process rather than a thermal pyramidal inversion.[7,36] However, the temperature range where the exchange process is observed to occur rapidly on the nmr time scale is still above that considered in the present study. Furthermore, the diastereotopic[32] nature of the isopropyl methyl groups in the spectrum of chloro(diisopropylamino)phenylphosphine at ambient temperature (Figure 1) is best attributed to a stable phosphorus pyramid on the nmr time scale.
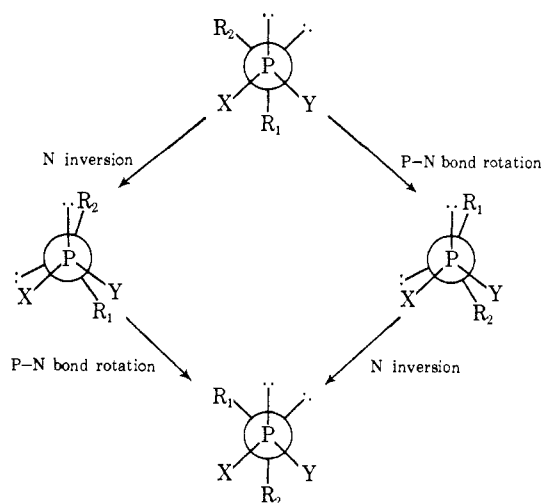
The problem therefore is to assess the relative importance of nitrogen inversion and torsion around the P–N bond. The following projection formulas

(34) J. B. Lambert, G. F. Jackson, and D. C. Mueller, J. Amer. Chem. Soc., **90,** 6401 (1968).
(35) L. Horner and H. Winkler, Tetrahedron Lett., 461 (1964).
(36) B. Fontal and H. Goldwhite, Tetrahedron, **22,** 3275 (1966).

indicate why, within the context of the nmr time scale, rapid nitrogen inversion and P–N bond rotation are both necessary to render the nitrogen substituents equivalent with respect to their chemical shifts (isochronous).[32] In the series of interconversions de-

picted above there are two distinct rate processes and consequently two distinct transition states. Unless the activation energies are of comparable magnitude, a physical probe, such as an nmr experiment, will only provide information about the process with the larger activation energy. *A priori* it is not possible to decide upon the relative magnitudes of the nitrogen inversional and P–N torsional barriers. The difficulty is partly due to the unknown effect of the phosphorus lone pair electrons on the nitrogen inversional barrier. Thus in certain acyclic compounds of the type R$_2$NX, the presence of a heteroatom, X, which contains one or more lone pairs of electrons, has been shown to augment the nitrogen inversional barrier, presumably because of lone pair–lone pair repulsion.[4d,f,g,9a,13a,b,11] On the other hand torsional barriers have been used to explain nmr spectral nonequivalence in acyclic sulfinamides,[10] sulfenamides,[11] N,N,O-trialkylhydroxylamines,[9c] and hydrazines.[4e,g]

In the case of the acyclic aminophosphines two arguments suggest that P–N bond torsion is the rate-determining step. Consider first the effect on the activation energies and coalescence temperatures of increasing the steric bulk of the nitrogen substituents. If pyramidal inversion at nitrogen were the rate-controlling step, an increase in steric bulk should lead to more pronounced congestion in the ground state and a concomitant *decrease* in activation energy and increase in rate (steric acceleration). Conversely, the PN torsion should show an *increase* of activation energy, *i.e.*, steric deceleration, when bulkier groups are present, because of increased steric congestion in the transition state (**3**). Clearly our data (Table I) imply that P–N bond torsion is the rate-determining process in the systems studied here.

A second line of evidence concerns the low-temperature pmr spectra of 2,2-dimethyl,1-diphenylphosphinoaziridine (**4**) (Figure 2). This compound was selected
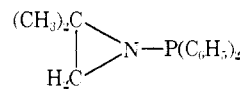

4

for study because the constraints of the three-membered aziridine ring are known to slow the rate of nitrogen inversion[37] sufficiently for it to be measured by nmr techniques. Moreover the attachment of heteroatoms such as chlorine[13a] or nitrogen[13b] to the aziridine nitrogen leads to a further enhancement of the nitrogen inversional barrier. Indeed, the nitrogen pyramid in certain N-chloroaziridines is too stable to permit the isolation of isomers.[38] It was, therefore, rather surprising that we were able to detect only broadening of the methyl and methylene protons of **4** down to −150°. Apart from the unlikely possibility that the chemical shifts of the methyl and methylene sites are accidentally degenerate, this would place an upper limit of ∼6 kcal/mol on the nitrogen inversional barrier in **4**. It therefore seems almost certain that the nitrogen inversional barrier in acyclic aminophosphines is even smaller and that the nitrogen atom is inverting rapidly on the nmr time scale throughout the temperature ranges used here. Note that a very small nitrogen inversional barrier has also been reported[15] for 1-diphenylphosphinoxyaziridine(**5**). Our results show, however, that the small barrier in **5** must be due not to the

$$H_2C \diagdown$$
$$\qquad \diagup NP(C_6H_5)_2$$
$$H_2C \diagup \quad \overset{O}{\overset{\|}{}}$$

5
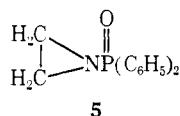
absence[15] of lone pair electrons on phosphorus, but rather to pπ–dπ bonding.

(b) Conformations of the Aminophosphines at Low Temperature. With the exception of $(CH_3)_2NPF_2$ (see later) the ground-state geometries of aminophosphines are not known in detail. In discussing the stereochemistry of these compounds it will be assumed that the nitrogen and phosphorus atoms are both tetrahedral. The conclusions would in any case be substantially unaltered if a different mode of hybridization of nitrogen were adopted. The six relevant structures of an aminophosphine, R_2NPXY, are then the *trans* (**6**), two *gauche* (**7** and **8**), and three eclipsed (**9, 10,** and **11**) conformers.
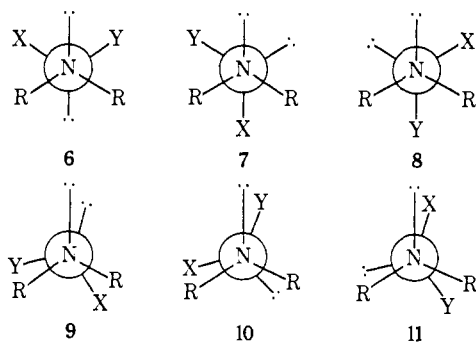
Several independent reports[5–8] have established that the R groups of unsymmetrical aminophosphines, R_2NPXY with X ≠ Y, become diastereotopic[32] at low temperatures. However, these observations do not in themselves provide any information concerning the conformations of aminophosphines at low temperatures because the environments of the R groups are

(37) A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5126 (1956).
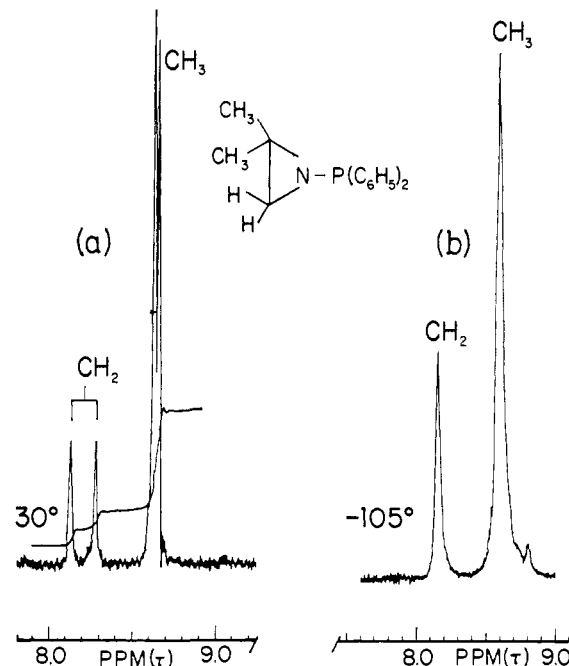
(38) S. J. Brois, *ibid.*, **90**, 508 (1968).

Figure 2. Proton nmr spectra of 2,2-dimethyl-1-diphenylphosphinoaziridine (**4**): (a) 60-MHz spectrum of a $CDCl_3$ solution at ambient temperature; (b) 100-MHz spectrum of a $CHFCl_2CF_2Cl_2$ solution at −105° with irradiation at the ^{31}P frequency.

different in each of the six conformers **6–11**. We therefore decided to study the stereochemistry of symmetrically substituted aminophosphines, *i.e.*, with X = Y. Prior to this work Imbery and Friebolin[7] had examined several such compounds and noted that the N-alkyl groups retain their chemical shift equivalence to −80°. On this basis it was concluded that the symmetrical aminophosphines adopt the *trans* conformation, **6**, at low temperatures. However, a curious feature in this paper was the fact that the benzyl methylene protons in the compounds $(C_6H_5CH)_2$-$(CH_3)NPX_2$, X = C_6H_5 or Cl, remained isochronous at −80°. Subsequently it has been found[39] that the methylene protons of $(C_2H_5)_2NPX_2$ and $(C_6H_5CH_2)_2$-NPX_2, X = C_6H_5 or Cl, remain isochronous under these conditions. Barring the unlikely possibility that the protons within each methylene group of the above compounds are accidentally equivalent, these observations refute the conclusion of Imbery and Friebolin[7] because the methylene protons should be diastereotopic in the *trans* conformation **6**. This in turn suggests that P–N bond rotation is still rapid on the nmr time scale at −80° in the case of the symmetrical aminophosphines, a suggestion confirmed by our experiments with $(CH_3)_2NPCl_2$ and $(CH_3)_2NP(CF_3)_2$ at temperatures below −100°. In both cases the presence of diastereotopic methyl groups was indicated by the presence of a pair of doublets in the pmr spectra[40] (Table II). These observations rule out the *trans* conformer **6** and one of the eclipsed conformers, **9**. In the case of the symmetrical aminophosphines, *i.e.*, X = Y, the eclipsed conformers **10** and **11** are equivalent, and the *gauche* forms **7** and **8** are spectroscopically identical in achiral solvents. While the present evi-

(39) W. R. Jackson, unpublished observation.

(40) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 1085 (1970).

dence does not distinguish between the *gauche* forms **7** or **8** and the eclipsed form **10** or **11**, the latter can probably be excluded on steric grounds. The *gauche* conformation therefore seems the best representation of the ground state geometry of acyclic aminophosphines. This conclusion is supported by a recent X-ray structure determination of $(CH_3)_2NPF_2$[41] which indicates that this compound adopts conformation **12** in the solid state at $-110°$. Conformation **12** differs from the *gauche* con-

12
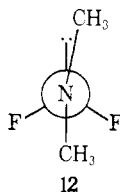
formations **7** and **8** only in that the hybridization of nitrogen has changed from sp^3 to sp^2. Indeed, conformation **12** is probably the best representation of the ground state geometry of an acyclic aminophosphine, given that the nitrogen atom is apparently inverting rapidly on the nmr time scale even at low temperatures so that the time-averaged geometry about this center is planar.

(c) Coupling Constants. Nuclear spin coupling constants are known to be sensitive to the stereochemical environment.[6] For instance two PCH couplings of opposite sign have been observed in a conformationally rigid cyclic phosphine,[42] and two different PCCH couplings are observed[43] in $(i-C_3H_7)_2PC_6H_5$ corresponding to the diastereotopic methyl groups. Two different PNCH couplings should therefore be observed at lower temperatures with $(CH_3)_2NPXY$ because the methyl environments in conformations **12, 7,** or **8** are nonequivalent. The coupling constants for the aminophosphines are presented in Tables I and II. Since in each case the value of J_{PNCH} at ambient temperature is the average of the two values (J_{PNCH} and J'_{PHCN}) at low temperatures, the latter must be of the same sign (and probably positive).[44] As to the assignment of the two different PNCH couplings to the two different methyl groups in **12**, our sole and rather tenuous argument is based on the low-temperature pmr spectrum of $CH_3ND \cdot P(CF_3)_2$ (we have shown[40] that the previous[45] interpretation of the variable-temperature nmr spectra of $CH_3NH \cdot P(CF_3)_2$ is incorrect). A pair of doublets is observed below $-120°$ with $J_{PNCH} = 13.9$ Hz, and $J'_{PNCH} \approx 4$ Hz. The ratio of the intensities of the doublets is *ca.* 4:1 with the more abundant rotamer having the larger coupling constant. Steric considerations suggest that the more abundant isomer should be **13**; if so, the larger PNCH

13
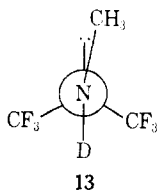
(41) E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1672 (1969).

(42) D. Gagnaire, J. B. Robert, and J. Verrier, *Chem. Commun.*, 819 (1967).

(43) W. McFarlane, *ibid.*, 229 (1968).

(44) S. L. Manatt, G. J. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

(45) N. N. Greenwood, B. H. Robinson, and B. P. Straughan, *J. Chem. Soc., A*, 230 (1968).

coupling constant in aminophosphines may be ascribed to the methyl group *cis* to the phosphorus lone pair electrons.

(d) Origins of the P–N Torsional Barriers. Three factors could contribute to the torsional barriers in aminophosphines, *i.e.*, steric effects, lone pair–lone pair repulsions, and nitrogen → phosphorus $p\pi$–$d\pi$ bonding.

The importance of steric effects is apparent from the data in Table I which show that the torsional barrier increases quite markedly with increasing size of the groups attached to nitrogen. Since the groups in question are electronically similar, the effect must be steric in origin, due presumably to crowding in the transition state.

The importance of lone pair repulsions seems to be indicated by the fact that the aminophosphines considered here seem to have *gauche* conformations. As **14** shows, the angle between the phosphorus lone pair

14
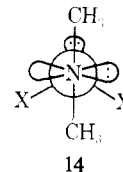
(arbitrarily assumed to be tetrahedrally hybridized) and the nitrogen lone pair in a pure 2p orbital is 90°. The preferred orthogonality of lone pair electrons is also apparent in compounds with N–N,[4] N–S,[11] O–O,[46] and S–S[47] bonds. The situation is admittedly complicated by the observed[41] phosphorus bond angles in $(CH_3)_2NPF_2$ which are close to 90°, implying, according to simple-minded MO theory, that the phosphorus atom is almost unhybridized and that the lone pair electrons consequently are in an orbital which is almost pure $3s$; if so, the lone pair repulsions would show almost no angular dependence. However, a recent *ab initio* SCF LCAO–MO calculation[48] on PH_3 indicates that the phosphorus lone pair orbital has considerable p character, so the N–P lone pair repulsions should in fact be directional.

The role of $p\pi$–$d\pi$ bonding is harder to establish; however, there are three observations which cannot be ascribed to lone pair repulsions or steric effects and which may reflect π bonding.

Consider first the torsional barriers for $(CH_3)_2NPCl_2$, $(CH_3)_2NP(CF_3)Cl$, and $(CH_3)_2NP(CF_3)_2$ (Tables I and II). If steric effects and/or lone pair repulsions were predominant, then the rotational barrier for the unsymmetrical compound $(CH_3)_2NP(CF_3)Cl$ should be intermediate between those of $(CH_3)_2NPCl_2$ and $(CH_3)_2$-$NP(CF_3)_2$. This is clearly not the case. All the symmetrical compounds studied (both here and elsewhere[7]) possess appreciably smaller rotational barriers than the unsymmetrical ones. Possibly the $p\pi$–$d\pi$ contribution to the torsional barrier is enhanced in the unsymmetrical compounds by an asymmetry induced in the P(3d) orbitals by virtue of the differing substituents on phosphorus.

(46) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261, 2276 (1967).

(47) O. Foss in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 8, and papers therein.

(48) J. M. Lehn and B. Munsch, *Chem. Commun.*, 1327 (1969).

The second argument for a $p\pi$–$d\pi$ interaction is provided by the work of Goldwhite and Rowsell,[8] who noted that compounds with widely differing phosphorus substituents, such as $CHCl_2CF_2P(Cl)N(CH_3)_2$ and $(CH_3)_2CHP(Cl)N(CH_3)_2$, had very similar coalescence temperatures. If the barrier were due to lone pair–lone pair repulsions, the coalescence temperatures would be expected to differ because the substituents should affect the phosphorus lone pair electrons to differing extents. And finally, our inability to observe torsional barriers in $(CH_3)_2NP(C_6H_5)_2$ and $(C_2H_5)_2NP(C_6H_5)_2$ cannot be explained in terms of steric effects and lone pair interactions and so must be attributed to π bonding.

Several other pieces of evidence also seem to point to the importance of $p\pi$–$d\pi$ bonding in aminophosphines. Thus the planar geometry of nitrogen, and the short PN bond length, in $(CH_3)_2NPF_2$[41] imply that the nitrogen atom is sp^2 hybridized; if so, the π interaction between nitrogen and phosphorus must be very strong.[29] A similar situation seems to hold in $(CF_3)_2P^{15}NH_2$ where the scalar ^{15}N–^1H coupling is 86.5 Hz.[49] This corresponds to ca. 31% s character in the nitrogen 2s orbital, implying that the hybridization of nitrogen is close to sp^2. Neither of these observations throws light on the possible angular dependence of $p\pi$–$d\pi$ bonding and it has indeed been generally supposed that this is small;[30] however, this supposition is based on the assumption that the 3d orbitals are entirely independent of the 3s and 3p and are not used in σ bonding. However, if the 3d orbitals have energies low enough to be used at all in bonding, they must contribute to all the bonds. If the PN bond is taken as the Z axis, and if the contributions of d_{zz} and d_{yz} orbitals to the σ bonds are unequal, then their availability for π bonding will also differ; in this case the strength of the $p\pi$–$d\pi$

bond to nitrogen will depend on the angular orientation of nitrogen and phosphorus. The reason why this point has been overlooked is that no such situation arises in the case of $p\pi$–$p\pi$ bonding, for here the π and σ orbitals differ in symmetry and so cannot mix. This is not true in the case of $p\pi$–$d\pi$ bonds since molecules containing them cannot have symmetries that lead to a separation of d orbitals from s and/or p.

(e) The Arsenic–Nitrogen Torsional Barrier in C_6H_5-$AsClN(CH_3)_2$. Since we have studied only one aminoarsine, we cannot be sure that the activation parameters refer to torsion about the As–N bond. However, analogy with the corresponding phosphine, $C_6H_5PClN(CH_3)_2$, certainly suggests that this is so and the observed barrier (8.2 kcal/mol) seems in any case too large to be attributed to nitrogen inversion. Barriers of this magnitude have, it is true, been observed in acyclic hydrazines;[4d,f,g] however, the longer central bond in aminoarsines, coupled with the possibility of $p\pi$–$d\pi$ bonding, would be expected to lower the barrier. If these arguments are accepted, the As–N rotational barrier in $C_6H_5AsClN(CH_3)_2$ is then 2.5 kcal/mol smaller than that in the analogous aminophosphine. The difference may be partly due to diminished steric and lone pair–lone pair interactions, the As–N bond being larger than the P–N bond; however, it is also possible that the π-type interaction between a 2p orbital of nitrogen and a 4d orbital of arsenic may be less than the corresponding 2p(N)–3d(P) interaction in an aminophosphine. The scalar ^{15}N–^1H coupling in $(CF_3)_2As^{15}NH_2$ (76 Hz[50]) is indeed much less than that (86.5 Hz) in the corresponding aminophosphine, the former value corresponding to about 27% s character in the nitrogen orbital and so implying a hybridization close to sp^3.

(49) A. H. Cowley, J. R. Schweiger, and S. L. Manatt, unpublished observations.

(50) Cf. M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, J. Chem. Soc., 2423 (1960).