A Study of the Conformation of 2-Dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes by Dynamic ^{13}C NMR and ^{15}N NMR[1]

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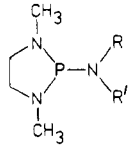
Abstract: ^{13}C NMR studies on the title compounds have succeeded in freezing out rotation around the exocyclic P-NR_2 bond at low temperatures. The preferred conformation has one N-R group syn to the phosphorus lone pair, and the other lies across the face of the diazaphospholane ring. The barriers to rotation around the exocyclic P-N bond are 8.1 and 10.1 kcal mol^{-1} for R = CH_2CH_3 and $CH(CH_3)_2$, respectively. $^1J_{PN}$(exo) is much larger than $^1J_{PN}$(endo). The stereochemical dependence of this coupling constant may reflect differences in the P-N conformation, although other explanations are considered.

Introduction

Recently there has been considerable interest in the structure and conformation of trisaminophosphorus(III) compounds.[3] Many of these investigations have been concerned with hexamethylphosphorous triamide, although its conformation is still not firmly established. Electron diffraction data appear to indicate a C_3 conformation,[3g] whereas UV photoelectron spectroscopic investigations[3a,b,f] favor a C_s conformation. There has been little application of ^{13}C NMR in this area, yet the known stereochemical dependence of phosphorus–carbon coupling constants[4] should make ^{13}C NMR a very useful conformation probe. ^{15}N NMR also holds promise in this area,[3c,5] particularly if a conformational dependence of ^{31}P, ^{15}N coupling can be established. We now report on a detailed ^{13}C and ^{15}N NMR study of the conformation and stereodynamics of a series of 2-dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes, **1–4.**

Results

^{13}C NMR Spectra. Ambient-temperature proton-decoupled ^{13}C NMR spectra of diazaphospholanes **1–4** showed doublet



1	R, R′ = CH_3
2	R, R′ = CH_2CH_3
3	R, R′ = $CH(CH_3)_2$
4	R = CH_3, R′ = $CH(CH_3)_2$

signals for each carbon due to phosphorus coupling (Figure 1). In compound **3** (Figure 1) off-resonance (gated) ^1H decoupling allowed $^1J_{CH}$ coupling to be observed yielding triplet signals for the ring CH_2's, doublets for the exocyclic methine carbons, and quartets for both the ring *N*-methyls and the isopropyl methyls. Signals in compounds **1, 2,** and **4** were assigned by their analogous positions. Chemical shifts and ^{31}P–^{13}C coupling constants are tabulated in Table I. The cyclic methylene carbons resonate at lowest field (δ ~53), close to the analogous signal in *N*-methylpyrrolidine (δ ~56.7).[6] The PNC coupling constants differ markedly for the three types of nitrogen-bonded carbons. Off-resonance ^1H irradiation experiments[4a] demonstrated that $^2J_{PNC}$ for the ring methylene carbons is negative, whereas the $^2J_{PNC}$ values for the endocyclic *N*-methyl carbons and the exocyclic *N*-alkyl carbons are positive. These conclusions are based on the results of a previous ^1H NMR study[3d] of **1** and other diazaphospholanes which indicated that the various PNCH couplings have the same sign and are positive.[7] The terminal methyl carbons of the dialkylamino groups in **2–4** showed three-bond couplings to phosphorus similar to those previously observed for other aminophosphorus(III) compounds.[4e-h]

At low temperature (below −100 °C for **1** and **2** and below −30 °C for **3**) a dramatic change was observed in the signals for the exocyclic *N*-alkyl groups, but signals from the ring methylene carbons and the methyls attached to the endocyclic nitrogens remained essentially unchanged in both chemical shifts and coupling to phosphorus. In compounds **1–3** each of the signals for the exocyclic *N*-alkyl carbons separated into two components of essentially equal intensity. Figure 1 illustrates this for compound **3.** The signal for the isopropyl methine carbons (δ 45.0, $^2J_{PNC}$ = +9.3 Hz at 25 °C) separated into two doublets (δ 46.8 and 42.5, $^2J_{PNC}$ = −8.8 and +26.0 Hz, respectively, at −116 °C). The signals for the isopropyl methyls exhibited similar behavior; the original doublet (δ 24.9, $^3J_{PNCC}$ = +8.0 Hz at 25 °C) was replaced by two doublets (δ 21.7 and 27.7, $^3J_{PNCC}$ < 5 and +14.8 Hz at −116 °C). An examination of Table I shows that an analogous result was obtained for compounds **1** and **2,** although the signals of the dimethylamino carbons of **1** did not allow accurate measurement of the two $^2J_{PNC}$ values because of residual signal broadening and overlap of the ring methyl signals.

The unsymmetrically substituted compound, **4,** exhibited considerable broadening of the three doublets emanating from the exocyclic methyl isopropylamino substituent as the temperature was lowered below −100 °C. At −120 °C three sharp doublets reemerged. These had slightly different chemical shifts and significantly different $^2J_{PNC}$ values compared to those observed at higher temperature and are assigned to a dominant rotamer (vide infra). The signals from the minor rotamer were not clearly visible, presumably because of residual exchange broadening and overlap with the signals of the major species. A small broadened signal at δ 31.6 (−125 °C) was observed. This is thought to be the high-field component of the exocyclic NCH_3 doublet from the minor rotamer. The population of this less stable form is estimated to be 15–20% from the weighted average $^2J_{PNC}$ for the methyl and methine carbons observed at −3 °C as compared to the major species couplings observed at −125 °C.[8]

^{15}N NMR Spectra. Proton-decoupled ^{15}N NMR spectra of compounds **1–4** showed two doublet signals with an intensity ratio of approximately 2:1 (Figure 2). The observed chemical shifts and coupling constants are tabulated in Table II. The less intense signal at low field can be assigned to the single exocyclic nitrogen as confirmed by the normal[9] downfield shift observed on changing the *N*-alkyl substituents from methyl to ethyl to isopropyl. The more intense doublet exhibited a smaller and opposite trend (Table II).

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Table I. ^{13}C Chemical Shifts (δ_C) and $^{31}P,^{13}C$ Coupling Constants (J) for 2-Dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes[a]

compd	temp, °C	ring NCH_3 δ_C, ppm	ring NCH_3 $^2J(PNC)$,[b] Hz	ring NCH_2 δ_C, ppm	ring NCH_2 $^2J(PNC)$,[b] Hz	exo NC δ_C, ppm	exo NC $^2J(PNC)$,[b] Hz	exo $NCCH_3$ δ_C, ppm	exo $NCCH_3$ $^3J(PNCC)$, Hz
1	−20	34.8	+21.5	53.6	−8.8	37.5	+16.6		
	−138	35.5	+22.0	54.3	−9.1	37.4, 39.0	br, ~50		
2	−50	34.5	+22.0	52.9	−9.2	39.2	+18.9	15.4	1.8
	−128	34.8	+20.8	52.7	−9.2	37.0, 39.6	−9, +48	14.0, 16.0	<5, <5
3	25	34.5	+23.6	52.8	−8.8	45.0	+9.3	24.9	8.0
	−116	34.7	+21.5	52.4	−8.8	46.8, 42.5	−8.2, +26.0	21.7, 27.7	<4, 14.8
4	−3	34.5	+22.0	53.3	−9.2	26.5,[d] 48.1[e]	<2,[d] +38.5[e]	22.1	4.3
	−125[f]	35.1	+21.4	53.5	br[c]	25.9,[d] 48.7[e]	−9.2,[d] +50.7[e]	22.3	<8

[a] Determined in $CHCl_2F$ solution (for **1**, **2**, and **4**) or in CH_2Cl_2 (for **3**) containing ~10% CD_2Cl_2 or $(CD_3)_2CO$ as internal lock; digital resolution 0.6 Hz (0.04 ppm). [b] Relative signs were determined on compound **2** and those cited for the other compounds are inferred. [c] Broad signal with unresolved coupling. [d] Methyl carbon. [e] Isopropyl methine carbon. [f] Data refer to the predominant PN rotamer; signals from the minor rotamer were too weak to assign (see text).

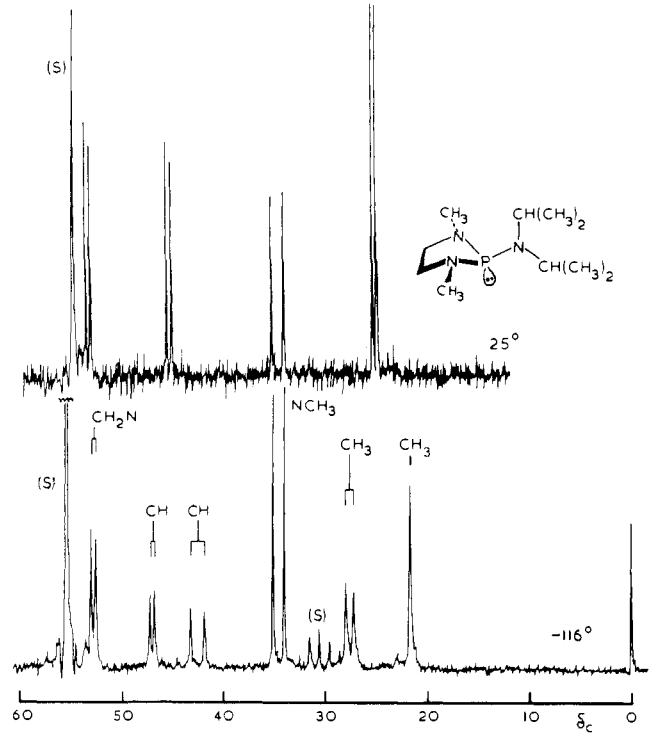
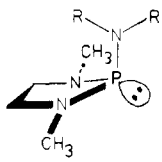


Figure 1. ^1H decoupled ^{13}C NMR spectra of **3** recorded at 25 (top) and −116 °C (lower). The signals marked (s) are from CH_2Cl_2 (δ ~56) and $(CD_3)_2CO$ (δ ~31). Chemical shifts are in parts per million from Me_4Si.

Discussion

Conformation around the Exocyclic PN Bond. The observation of nonequivalent N-alkyl groups at low temperature indicates that the exocyclic P–N bond rotation has become slow on the NMR time scale. The frozen ground-state conformation (ignoring the ring conformation, vide infra) is that depicted in **5** where the exocyclic N-alkyl groups are oriented syn and anti to the phosphorus lone pair. Conformation **6**,



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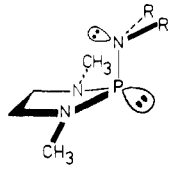

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which has been previously proposed[3c] as the ground-state conformation of **1**, is excluded since the N-alkyl groups would be equivalent. Although these data cannot confirm this assumption, a planar geometry at the exocyclic nitrogen would be expected since ab initio molecular orbital calculations[10] and X-ray crystallographic studies[11-13] on acyclic monoaminophosphorus compounds give planar geometry at nitrogen and a ground-state conformation in which the phosphorus and nitrogen lone pair axes are orthogonal. However, molecular orbital calculations[10] on PH_2NH_2 indicate that the nitrogen atom may become pyramidal as the dihedral angle between the lone pairs is changed away from the preferred value of 90°.

Table II. ^{15}N NMR Data for 2-Dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes[a]

compd	endo δ_N,[b] ppm	endo $^1J_{PN}$,[c] Hz	exo δ_N,[b] ppm	exo $^1J_{PN}$,[c] Hz
1	−343.4	52	−332.8	90
2	−345.7	52	−302.7	92
3	−353.8	51	−286.0	96
4	−345.5	51	−308.7	90

[a] Determined as ca. 50% solutions in C_6D_6 (for **1**, **2**, and **4**) or in CD_2Cl_2 (for **3**). [b] Chemical shifts are relative to external $CH_3{}^{15}NO_2$; digital resolution 0.015 ppm. [c] Digital resolution 0.6 Hz.

The markedly different PNC coupling constants for the nonequivalent N-alkyl groups (Table I) further confirm that compounds **1–4** adopt conformation **5**. Previous investigations of other tervalent phosphorus–nitrogen compounds have established that $^2J_{PNC}$ is very sensitive to the PN conformation and is large and positive (25–40 Hz) for an N-alkyl group syn to the phosphorus lone pair and smaller negative (−7 to −13 Hz) for an anti N-alkyl group.[4a,c,i] The large positive syn coupling arises from direct overlap between the phosphorus lone pair orbital and antibonding orbitals of the neighboring alkyl group.[14] The data in Table I show a shift reversal for the syn and anti NC signals. Thus the syn carbon is at lower field than the anti carbon in the dimethyl (**1**) and diethyl (**2**) compounds and at higher field in the diisopropyl analogue (**3**). A comparison of the published[4a,c] low-temperature ^{13}C NMR data for $PhP(Cl)NMe_2$ and $PhP(Cl)N(CHMe_2)_2$ indicates a similar reversal of the relative syn and anti NC chemical shifts, which are syn downfield and syn upfield, respectively. The rather low value of $^2J_{PNC}$ = +26 Hz for the syn NCH carbon in the diisopropyl compound (**3**) as compared with $^2J_{PNC}$ ~ +48 Hz for the syn NCH_3 or NCH_2 carbons in **1** or **2** also parallels the situation in $PhP(Cl)NMe_2$ and $PhP(Cl)N(CHMe_2)_2$ where $^2J_{PNC}$ (syn) is +34 and +25 Hz, respectively.[4a,c]

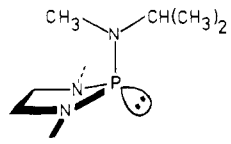
The exo PNC coupling constants for the unsymmetrically substituted compound (**4**) clearly establish that the predomi-

Table III. Dynamic ^{13}C NMR Data for Exocyclic P-N Bond Rotation

compd	temp, °C	obsd signals	k, s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}
2[a]	−109	NCH_2	51.5	8.13
	−109	CH_3	50.0	8.14
3[b]	−46	NCH	905	10.10
	−46	$(CH_3)_2$	916	10.10

[a] In $CHCl_2F$. [b] In CH_2Cl_2.

nant PN conformer is **7** rather than **8** since the isopropyl methine carbon shows a large positive coupling and the *N*-



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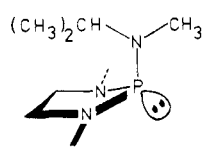

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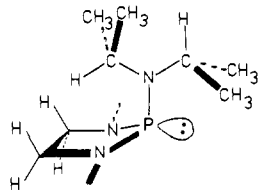
methyl group has a negative $^2J_{PNC}$. Conformer **8** will be somewhat destabilized by nonbonded interactions between the isopropyl group and the methylene hydrogens on the diazaphospholane ring. It is interesting that $^2J_{PNC}$ for the syn methine carbon in **7** (+50.7 Hz) is considerably larger than the analogous value (+26.0 Hz) in the diisopropyl compound **3**, and close to $^2J_{PNC}$(syn) in **1** and **2**. The anomalously low $^2J_{PNC}$(syn) for the isopropyl methine carbon in **3** [and in $Ph(Cl)PN(CHMe_2)_2$][4c] is therefore not a consequence of the *gem*-dimethyl substitution, but arises from the presence of the second isopropyl group on the nitrogen atom. Steric interactions between the isopropyl groups in **3** will probably impart a marked conformational preference around the N-CH bonds such that the syn methine proton is directed away from the phosphorus lone pair as depicted in **9**. Indeed a recent X-ray crystallographic study on $Ph(Cl)P(O)-N(CHMe_2)_2$ has shown an isopropyl arrangement of this type.[13]



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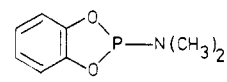

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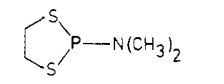

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The overlap between the phosphorus lone pair orbital and vacant antibonding C-C or C-H orbitals involving the syn methine carbon may be less favorable in this N-CH arrangement, and hence $^2J_{PNC}$ is less positive. Furthermore, conformation **9** places the syn isopropyl methyl groups close to the phosphorus lone pair, and this could account for the unusually large three-bond PNCC coupling of 14.8 Hz observed for one of the isopropyl groups (presumably syn) in the frozen spectrum.

The P-N rotational rate constants in **2** and **3** were evaluated by analysis of the NC and terminal CH_3 band shapes in the region of gross exchange broadening (Table III). The free-energy barriers determined from both sets of signals are in excellent agreement. The P-N rotational barrier in **2** is close to those reported for compound **10** ($\Delta G^{\ddagger}$ = 7.8 kcal mol^{-1})[15] and **11** ($\Delta G^{\ddagger}$ = 7.6 kcal mol^{-1})[16]. The significantly higher barrier in the diisopropyl analogue **3** is to be expected on the basis of previous measurements of P-N rotational barriers, and indicates that the torsional transition state is more sterically hindered than the ground state.[7,10,17] It is interesting that

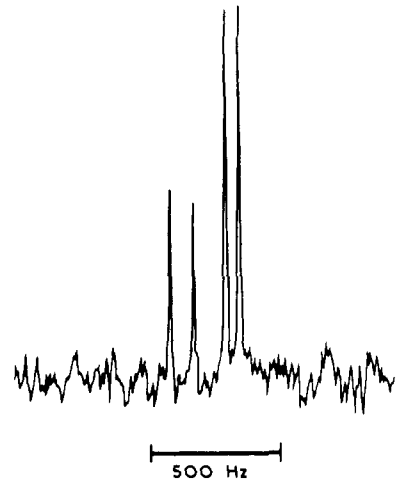
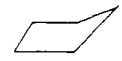


Figure 2. ^1H decoupled ^{15}N NMR spectrum of **1**, recorded at ambient temperature.

acyclic analogues $(Me_2N)_3P$ and $(Et_2N)_3P$ apparently remain conformationally mobile in the NMR time scale at temperatures where PN rotation in **1** and **2** has become slow.[3f] The difference in PN torsional behavior may be ascribed to the change in the ground-state conformation between the acyclic and cyclic compounds.

As discussed previously for other diisopropylaminophosphorus compounds,[17] the measured barrier in **3** could in principle refer to C-N rather than P-N rotation. A geared arrangement (**9**) of the isopropyl groups minimizes steric interactions, and, if rotation around the *N*-isopropyl bonds were frozen, the isopropyl groups would be nonequivalent even if P-N rotation were fast. However, even if this were the case, the exocyclic PNC coupling constants show that the P-N conformation is that shown in **9**. One of the P-N rotameric forms would then have to heavily predominate since $^2J_{PNC}$ for the anti N-CH is similar to the values found for other anti carbons ($J \sim -9$ Hz).

Conformation of the Diazaphospholane Ring. The observation that the PNC coupling constants for the cyclic methylene and ring methyl carbons remain essentially constant along the series **1**-**4** indicates that there is no major change in the ring conformation. A number of possible envelope (**12**) or



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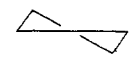

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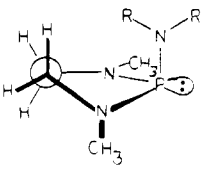
half-chair (**13**) conformations are possible.[18] In the former case either the carbon, nitrogen, or phosphorus can occupy the flap position and the exocyclic NR_2 substituent can be pseudoaxial or pseudoequatorial. In the half-chair conformation either the N-P-N, the P-N-C, or the N-C-C moieties can lie in the median plane. Precise conformational assignment is therefore difficult, and the situation is complicated by the possibility that more than one conformation might be appreciably populated. Nevertheless, the NMR data contain considerable conformational information.

The ^1H NMR spectrum of **1** has been previously analyzed by Robert and co-workers.[3d] The vicinal HCCH coupling constants for the cyclic methylene protons ($^3J_{AA'}$ = 6.5, $^3J_{BB'}$ = 7.3, $^3J_{AB'}$ = 6.0 Hz)[3d] are of comparable magnitude to the analogous couplings in 1,3-dioxa- and 1,3-dithiaphospholanes and indicate a CH_2-CH_2 torsional angle in the region 30-50°.[4g,19-22] Accordingly, the P-flap envelope and the NCC coplanar half-chair conformations in which the methylene protons are eclipsed can probably be excluded. The ^{13}C NMR

data show that $^2J_{PNC}$ for the cyclic methylene carbons (−9 Hz) is identical in sign and magnitude with $^2J_{PNC}$ for the anti exocyclic *N*-alkyl group. Therefore it would seem that the dihedral angle between the cyclic CH_2–N bonds and the phosphorus lone pair must be fairly close to 180°.[23] Additionally, the PNC and PNCH coupling constants for the ring *N*-methyl group (22 and 12.4 Hz, respectively) indicate a dihedral angle with the phosphorus lone pair in the general region of 45°.[4i] The above data are best accommodated in an N-flap envelope conformation **14** in which the exocyclic NR_2 substituent is pseudoaxial (anti to the flap). Conformation **14** is almost equivalent to a half-chair with the P–N–C system in the median plane, and can alternately be regarded as being derived from a P-flap envelope by twisting the CH_2–CH_2 system about 30° out of the eclipsed state. Rapid pseudorotation of the ring will interconvert this conformation with its enantiomer where the other nitrogen occupies the flap position.



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^{15}N NMR Spectra. The most interesting aspect of the ^{15}N NMR is the finding that the exocyclic PN coupling constant is almost twice the magnitude of the endocyclic $^1J_{PN}$. This observation is surprising since Gray and Albright[3c] have recently reported that the exocyclic PN coupling constant in compound **1** was 24.0 Hz. Proposals were advanced to account for this anomalously small coupling. The present determination of 90 Hz for this coupling constant is in good agreement with the other compounds in the series, and with the reported exocyclic $^1J_{PN}$ = 84.2 Hz in 2-anilino-1,3-dimethyl-1,3,2-diazaphospholane.[5] Hence, the exocyclic PN coupling is in fact unsually *large*. Two postulates can be advanced to explain the difference in the exo- and endocyclic coupling constants: (1) The cyclic N–P–N bond angle may be enlarged thereby reducing the s character in the exocyclic PN bond. Hence the reduced coupling ($^1K_{PN}$) would be more negative and $^1J_{PN}$ more positive for the exocyclic nitrogen. (This suggestion has also been made by McFarlane and Wrackmeyer.)[5] (2) $^1J_{PN}$ may be sensitive to the conformation around the PN bond, which differs for the exo- and endocyclic cases.

On the basis of the first suggestion, $^1J_{PN}$(endo) should be considerably smaller than $^1J_{PN}$ in an acyclic analogue on account of the increased s character in the endocyclic PN bonds. $^1J_{PN}$ in $(Me_2N)_3P$ (+59.1 Hz)[24] is indeed larger than the endocyclic coupling in **1**–**4**, but the difference is quite small. On the other hand, CNDO/2 FPT calculations on a model compound have indicated that *both* exo- and endocyclic $^1J_{PN}$ become more positive (larger) as the endocyclic NPN bond angle increases.[3c] The second suggestion is supported by the marked dependence of $^1J_{PP}$ in diphosphines on the dihedral angle between the vicinal lone pairs.[25] Furthermore, CNDO/2 FPT calculations on $(NH_2)_3P$ indicate that $^1J_{PN}$ does depend on the PN dihedral angle when the nitrogen is pyramidal, though apparently not when it is trigonal.[3c] However, it may be artificial to separate these conformational features since the ab initio calculations of Cowley and co-workers[10] on NH_2PH_2 suggest that the nitrogen may change from trigonal to pyramidal as the PN dihedral angle (ϕ) is twisted away from the preferred 90° ($\phi \sim 45°$ for the endocyclic nitrogen in **1**–**4**). A possible drawback with this postulate is that the endocyclic PN conformation, and hence the endo PN coupling, would seem to be anomalous with respect to simple acyclic aminophosphorus(III) compounds; yet the reported $^1J_{PN}$ values in Me_2PNHPh (53.0 Hz),[5] $(Me_3C)_2PNHPh$ (59.6 Hz),[5] $(CF_3)_2PNH_2$ (53.2 Hz),[26] and F_2PNH_2 (72.5 Hz)[27] are generally closer to the endocyclic coupling than to the exocyclic value. However, the data for F_2PNH_2 indicate that substituent effects are also important.

Further ^{15}N NMR studies and molecular orbital calculations on aminophosphorus(III) compounds may clarify the origin of the marked geometrical dependence of $^1J_{PN}$.

Experimental Section

Materials. Compounds **1**–**4** were prepared by reacting 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane with a 2 molar excess of the appropriate dialkylamine in dry ether under nitrogen.[28] After filtration and removal of the solvent, the resulting liquids were distilled: **1**, bp 30–32 °C (1.8 mm); **2**, bp 59 °C (2.4 mm); **3**, bp 70–72 °C (0.5 mm); **4**, bp 84 °C (8.8 mm). The ^{13}C and ^{1}H NMR spectra and mass spectra of these compounds were in accord with the structures. All compounds were handled carefully in view of a previous toxicity warning.[28]

NMR Spectra. ^{13}C NMR spectra were obtained at 15.03 MHz on a JEOL FX-60 Fourier spectrometer or at 20.0 MHz on a Varian CFT-20 instrument. Probe temperature was measured on a digital temperature indicator equipped with a copper–constantan thermocouple inserted into the sample at the level of the receiver coil. The ^{1}H irradiation induced currents in the thermocouple and was swtiched off just prior to reading the temperature. Solutions were freshly prepared since these aminophosphorus compounds reacted slowly with chlorinated solvents (rapidly in the case of CCl_4).[29] The relative signs of coupling constants (J_{PNC}) were established using the technique described by Wehrli et al.[4a] Exchange-broadened band shapes were converted to digital form and analyzed as four-site systems using the computer program INMR.[17] Standard deviations between calculated and experimental band shapes were less than 3%. ^{15}N NMR spectra were obtained at 18.24 MHz on a Bruker WB-180 instrument equipped with a 25-mm probe. Samples were not doped with relaxation agent, and typically 10 000–30 000 transients were accumulated with a pulse interval of 4 s and a flip angle of 30°.

Acknowledgments. The authors gratefully acknowledge financial support from the NATO Division of Scientific Affairs, and in part the Research Corporation (J.H.H. and S.D.W.). W.B.J. thanks the Science Research Council for an allocation of time on the Bruker WH-180 spectrometer at PCMU, Harwell for ^{15}N NMR studies. Special thanks are accorded to Dr. Ian Stenhouse for obtaining the ^{15}N spectra.

References and Notes

(1) Preliminary communication: J. H. Hargis, S. D. Worley, W. B. Jennings, and M. S. Tolley, *J. Am. Chem. Soc.*, **99**, 8090 (1977).
(2) (a) Auburn University; (b) University of Birmingham.
(3) (a) A. H. Cowley, D. W. Goodman, N. A. Kuebler, M. Sanchez, and J. G. Verakde, *Inorg. Chem.*, **16**, 854 (1977); (b) A. H. Cowley, R. E. Davis, M. Lattman, M. McKee, and K. Ramadna, *J. Am. Chem. Soc.*, in press; (c) G. A. Gray and T. A. Albright, *ibid.*, **99**, 3243 (1977); (d) J.-P. Albrand, A. Cogne, D. Gagnaire, and J.-B. Robert, *Tetrahedron*, **28**, 819 (1972); (e) A. Cogne, J.-B. Robert, and L. Wiesenfeld, *Chem. Phys. Lett.*, **57**, 627 (1978); (f) J. H. Hargis and S. D. Worley, *Inorg. Chem.*, **16**, 1687 (1977); (g) M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer, and E. Unger, *J. Chem. Soc., Dalton Trans.*, 1207 (1975); (h) K. Barlos, H. Noth, and B. Wrackmeyer, *Z. Naturforsch. B*, **33**, 515 (1978); (i) G. Bulloch, R. Keat, and D. G. Thompson, *J. Chem. Soc., Dalton Trans.*, 1044 (1977); (j) L. V. Vilkov, L. S. Khaikin, and V. V. Evdokinov, *Zh. Strukt. Khim.*, **10**, 1101 (1969).
(4) (a) M.-P. Simonnin, R.-M. Lequan, and F. W. Wehrli, *J. Chem. Soc., Chem. Commun.*, 1204 (1972); (b) G. A. Gray and S. E. Cremer, *ibid.*, 367 (1972); (c) J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *Tetrahedron Lett.*, 4919 (1973); (d) M. Haemers, R. Ottinger, D. Zimmerman, and J. Reisse, *ibid.*, 2241 (1973); (e) J. P. Dutasta and J. B. Robert, *J. Chem. Soc., Chem. Commun.*, 747 (1975); (f) M. D. Gordon and L. D. Quin, *J. Org. Chem.*, **41**, 1690 (1976); (g) W. G. Bentrude and H. W. Tan, *J. Am. Chem. Soc.*, **98**, 1850 (1976); (h) J. Martin, J. B. Robert, and C. Taieb, *J. Phys. Chem.*, **80**, 2417 (1976); (i) G. Bulloch, R. Keat, and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 764 (1978).
(5) W. McFarlane and B. Wrackmeyer, *J. Chem. Soc., Dalton Trans.*, 2351 (1976).
(6) E. Pretsch, T. Clerc, J. Seibl, and W. Simon, "Tabellen zur Strukturaufklarung Organischer Verbindungen mit Spektroskopischen Methoden", Springer-Verlag, New York, 1976.
(7) $^3J_{PNCH}$ is almost always positive in tervalent aminophosphorus compounds. See ref 4a; A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.*, **92**, 5206 (1970).
(8) In order to obtain the estimate of the population of the less stable rotamer, the $^2J_{PNC}$ coupling constants in this form were assumed to be the same

as those for the analogous carbons in compounds **3** and **1**. Thus for the methine carbon $(1 - x)(50.7\ Hz) = x(-8.2\ Hz) = 38.5$ Hz, and for the methyl carbon $(1 - x)(-9.2\ Hz) + x(50\ Hz) = 0$ Hz, giving estimates of 0.2 and 0.16 for the mole fraction (x) of the minor form.
(9) M. Witanowski and G. A. Webb, "Nitrogen NMR", Plenum Press, New York, 1973.
(10) I. G. Csizmadia, A. H. Cowley, M. W. Taylor, and S. Wolfe, *J. Chem. Soc., Chem. Commun.*, 432 (1974); A. H. Cowley, M. W. Taylor, M.-H. Whangbo, and S. Wolfe, *ibid.*, 838 (1976).
(11) E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1672 (1969).
(12) A. Grand, J. B. Robert, and A. Filhol, *Acta Crystallogr., Sect. B*, **33**, 1526 (1977), and references cited therein.
(13) K. Paxton and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 647 (1978), and references therein.
(14) W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Am. Chem. Soc.*, **94**, 8501 (1972), and references cited therein.
(15) M.-P. Simonnin, C. Charrier, and R. Burgada, *Org. Magn. Reson.*, **4**, 113 (1972).
(16) H. Boudjebel, H. Goncalves, and F. Mathis, *Bull. Soc. Chim. Fr.*, 628 (1975).
(17) J. Burdon, J. C. Hotchkiss, and W. B. Jennings, *J. Chem. Soc., Perkin Trans. 2*, 1052 (1976).
(18) For a detailed discussion of the possible conformations of phospholane ring systems see ref 4g.
(19) P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Am. Chem. Soc.*, **90**, 715 (1968).
(20) J.-P. Albrand, D. Gagnaire, J. Martin, and J.-B. Robert, *Org. Magn. Reson.*, **5**, 33 (1973).
(21) G. Y. Schultz, I. Hargittai, J. Martin, and J.-B. Robert, *Tetrahedron*, **30**, 2365 (1974).
(22) M. Revel, J. Roussel, J. Navech, and F. Mathis, *Org. Magn. Reson.*, **8**, 406 (1976).
(23) One must be a little cautious here since the cyclic methylene carbon can also couple to the phosphorus by a three-bond route, and this additional pathway could contribute to the $^2J_{PNC}$. However, the observation that the coupling constant is precisely equal to that for the exocyclic NC suggests that the three-bond route is not important.
(24) G. A. Gray and T. A. Albright, *J. Am. Chem. Soc.*, **98**, 3857 (1976).
(25) J.-P. Albrand, H. Faucher, D. Gagnaire, and J.-B. Robert, *Chem. Phys. Lett.*, **38**, 521 (1976); J.-P. Albrand, A. Cogne, and J.-B. Robert, *ibid.*, **42**, 498 (1976); J.-P. Albrand, J.-B. Robert, and H. Goldwhite, *Tetrahedron Lett.*, 949 (1976).
(26) A. H. Cowley, J. H. Schweiger, and S. L. Manatt, *Chem. Commun.*, 1491 (1970).
(27) D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1215 (1973).
(28) F. Ramirez, A. U. Patwardham, H. J. Kugler, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 6276 (1967).
(29) J. H. Hargis and W. D. Alley, *J. Am. Chem. Soc.*, **96**, 5927 (1974).

An Unusual Solvent Dependence of the Carbon-13 Nuclear Magnetic Resonance Spectral Features of Some Glycosides as Studied by Relaxation-Time Measurements[1]

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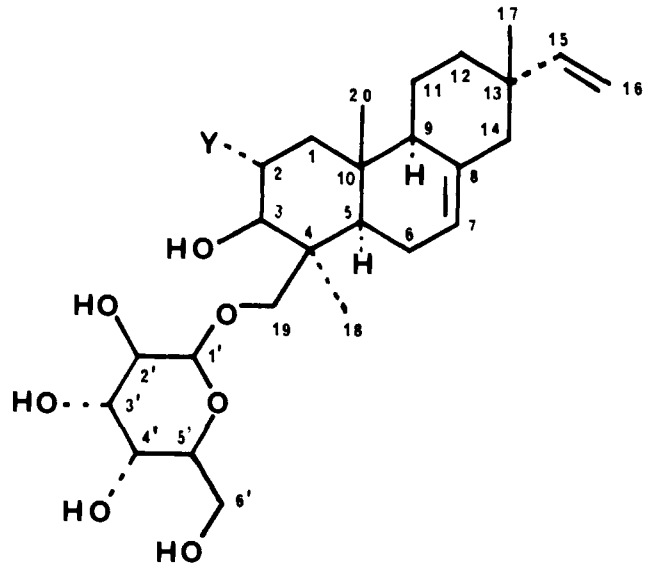
Abstract: The relaxation times of the carbon centers of virescenoside A and B, glycoside metabolites of the mushroom *Oospora virescens* (Link) Wallr., have been determined for different deuteriochloroform–methanol solvent mixtures. In the absence of methanol the ^{13}C NMR spectra show broad lines, corresponding to long correlation times and the presence of hydrogen-bonded intermolecular complexes. The methyl groups show a relationship between relaxation time and steric constraint, and the vinyl side chain reveals a connection of the T_1 values of its two carbons with its unique geometry.

The metabolites of the mushroom *Oospora virescens* (Link) Wallr. are isopimaradienic altrosides, the ^{13}C NMR spectral analysis of some aglycones of which have been reported.[3] Even though thus the carbon shifts of the aglycones virescenol A and B are on record,[3] their glycosides virescenoside A (**1a**) and **B** (**1b**) had to be ignored heretofore in view of their unusual spectral behavior. As Figure 1 indicates, the proton-decoupled ^{13}C NMR spectrum of a deuteriochloroform solution of virescenoside A is characterized by many broad, diffuse signals which sharpen into the customary singlets of narrow line width upon the addition of ca. 20 molar equiv of methanol. In order to gain insight into this phenomenon, it was decided to carry out a systematic study of the solvent dependence of the ^{13}C NMR spectral characteristics. Since the carbon relaxation times appeared to be a good NMR parameter for the assessment of the mechanism of the unusual effect, their measurement was initiated.



1a, Y = OH
b, Y = H

Experimental Section

The spectra of solutions of 500 mg of each virescenoside in 3 mL of deuteriochloroform–methanol mixtures, the deuteriochloroform having been filtered through basic alumina to avoid the presence of acid impurities, were recorded on a Varian XL-100-15 NMR spectrometer operating at 25.2 MHz in the Fourier transform mode. The methanol was added to the deuteriochloroform solutions in multiples of 1 molar equiv. The spectrometer probe temperature of 25, 35, or 50 °C was kept constant throughout any experiment. The T_1 values were obtained by the inversion-recovery method[4] and the pulse width

0002-7863/80/1502-0017$01.00/0