References and Notes

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(6) $J_{BD} = J_{BH} \times \gamma_D/\gamma_H$ = 83 Hz (obsd) × 1/6.514 = 12.74. See: F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, p 90.

A Tris(dialkylamino)phosphine with Pyramidal Nitrogens

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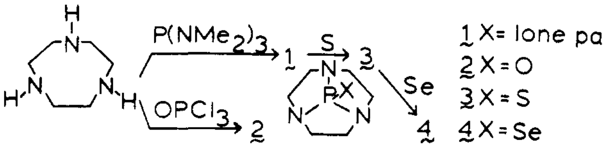
Abstract: Syntheses for the unstable symmetrical tricyclic aminophosphine **1** and its relatively stable O=P (**2**), S=P (**3**), and Se=P (**4**) derivatives are reported. The failure of **1** to form a stable BH_3 adduct contrasts with that observed for $P(NMe_2)_3$, $P(MeNCH_2)_3CMe$, and $P(\overline{NCH_2CH_2})_3$ and is rationalized in terms of electronic differences on the nitrogen which are imposed by structural constraints. The trend in ${}^1J_{PSe}$ for these compounds is shown to be consistent with this idea. The structure of **3**, determined by X-ray means, substantiates our earlier postulate that constraint in $P(ZC)_3$ systems decreases the PZC angle before the ZPZ angle is affected.

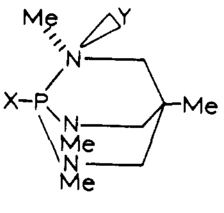
Introduction

Owing to the lack of unambiguous structural and PES data, the assignment of the conformational preference of acyclic tris(dialkylamino)phosphines remains unsettled.[1] Complicating this problem is the question of planarity or pyramidality of the nitrogens in the PNR_2 moiety. In the absence of steric factors, nitrogen is found from X-ray diffraction studies to be generally planar or nearly so (i.e., the sum of the angles around nitrogen is >355°) in PN<, O=PN<, and S=PN< systems.[2] Evidence that subtle steric and/or electronic forces may be operative can be seen in the 348° sum of the angles about nitrogen deduced from an electron diffraction study of Me_2NPF_2[3] (although microwave[4] and X-ray diffraction[5] work revealed a planar nitrogen) and in the <340° for the angle sum determined by X-ray means for one nitrogen in tris(morpholino)- and two nitrogens in tris(piperidinyl)phosphine.[6]

The preparations of the compounds in Scheme I were carried out in order (1) to examine a rigid tris(dialkylamino)phosphine **1** which might closely duplicate the C_{3v} structure proposed to be the dominant conformer of $P(NMe_2)_3$ on the basis of PES spectral studies,[7] (2) to assess the electronic consequences of forcing the nitrogen lone pairs to be cis to X in the compounds in Scheme I as opposed to their geometry in **5–9** wherein all the nitrogen lone pairs are orthogonal to P–X,[2,8,9] and (3) to further test[10] our hypothesis[11] that the ZPZ angles around a bridgehead phosphorus in $P(ZC)_3$ systems are not nearly so sensitive to constraint as are the PZC angles around the phosphorus substituent atom Z.

Scheme I





	X	Y		X	Y
5	ℓp	ℓp	9	H_3B	ℓp
6	O	ℓp	10	H_3B	BH_3
7	S	ℓp	11	S	BH_3
8	Se	ℓp	12	O	BH_3

Experimental Section

Materials. Solvents and reactants, unless specifically noted otherwise, were all reagent grade or better. Aromatic solvents, acetonitrile, and dimethylformamide were dried over 4A molecular sieves or alternatively with lithium aluminum hydride or NaK alloy for the aromatic solvents. Ethanol was removed from preserved chloroform by washing several times with half the volume of water, drying for at least 1 day over anhydrous calcium chloride, and distilling onto magnesium sulfate or 4A molecular sieves. Ether was dried with sodium, and methylene chloride with P_4O_{10}.

Tris(dimethylamino)phosphine (90+%), the borane adduct of tetrahydrofuran, diethylenetriamine, and *sym*-dimethylethylenediamine were obtained from Aldrich Chemical Co.; potassium borohydride and potassium superoxide were obtained from Alfa Inorganics; yellow mercuric oxide (NF, powder) was obtained from Mallinckrodt; nitrogen dioxide was obtained from Matheson; aziridine was obtained from Dow Chemical; tris(aziridinyl)phosphine oxide (80% solids in ethanol) was obtained from Polysciences, Inc. The last substance was distilled (82 °C, 0.1 mm) (caution) and recrystallized (benzene/petroleum ether, mp 43–44 °C, lit.[12] 41 °C) before use. Phosphorus trichloride, phosphorus oxychloride, thiophosphoryl chloride, and pyridine were distilled in a nitrogen atmosphere before use. Aziridine and triethylamine were stored over potassium hydroxide pellets. Ethylene glycol was stored over 4A molecular sieves. Practical grade *p*-toluenesulfonyl chloride was purified by precipitating impurities from a chloroform solution with petroleum ether.

Measurements and Procedures. All ${}^1H$ NMR spectra were obtained with a Varian A-60 or HA-100 spectrometer on solutions containing tetramethylsilane as internal standard. Analyses of ${}^1H$ NMR spectra were performed with the aid of the LAOCN III program[13] adapted for use in Iowa State's IBM 360/65-370/158 computer. ${}^{13}C$ and ${}^{31}P$ NMR spectra were obtained with a Bruker HX-90 spectrometer operating at 22.63 and 36.43 MHz, respectively, in the Fourier transform mode employing white-noise proton decoupling with deuterium of the deuterated solvent as a lock. Tetramethylsilane and 85% H_3PO_4 were used as internal and external standards, respectively, with downfield shifts considered positive. Coupling constants in the ${}^{13}C$ spectra are precise to +0.5 Hz.

A Beckman 4250 spectrometer was used to obtain infrared spectra which were calibrated with polystyrene. Mass spectra were obtained from an AEI MS-902 high-resolution spectrometer. Exact masses were determined by peak matching with standards. Melting points were obtained in open capillaries on a Thomas Uni-Melt apparatus and are uncorrected.

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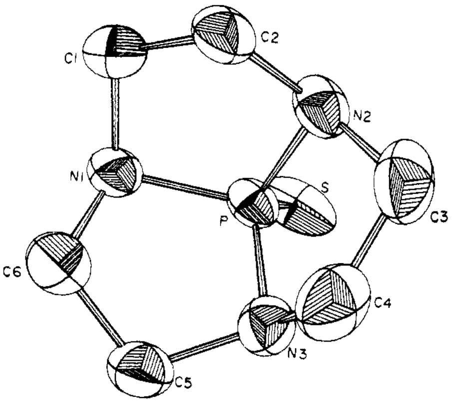


Figure 1. Computer drawing of molecular structure of **3**.

Table I. Intramolecular Bond Distances and Angles for **3**[a]

distances, Å		angles, deg	
P-S	1.919 (2)	S-P-N1	118.2 (2)
P-N1	1.682 (4)	S-P-N2	117.6 (1)
P-N2	1.694 (4)	S-P-N3	117.4 (2)
P-N3	1.680 (4)	N1-P-N2	100.0 (2)
N1-C1	1.490 (7)	N1-P-N3	100.0 (2)
N1-C6	1.489 (6)	N2-P-N3	100.1 (2)
N2-C2	1.483 (6)	N1-C1-C2	108.2 (4)
N2-C3	1.478 (8)	N1-C6-C5	106.4 (4)
N3-C4	1.488 (7)	N2-C2-C1	106.5 (4)
N3-C5	1.494 (7)	N2-C3-C4	108.2 (5)
C1-C2	1.517 (8)	N3-C4-C3	106.5 (4)
C3-C4	1.514 (8)	N3-C5-C6	107.8 (4)
C5-C6	1.518 (8)	C1-N1-C6	114.4 (4)
		C2-N2-C3	114.7 (4)
		C4-N3-C5	115.0 (4)

[a] Numbering of the atoms corresponds to that in Figure 1. Estimated standard deviations are given in parentheses for the least significant figures.

An approximately spherical crystal of **3** (+0.2 mm diameter) selected from a sample of **3** recrystallized from $CHCl_3/Et_2O$ was found to be monoclinic with a = 10.896 (1) Å, b = 11.443 (1) Å, c = 7.288 (1) Å, β = 104.45 (1)°, and four molecular units of **3** per unit cell. Systematic extinctions ($h0l$ absent if $h + l = 2n + 1$, $0k0$ absent if $k = 2n + 1$) identified the space group as $P2_1/n$.

A fully automated Hilger-Watts four-circle diffractometer equipped with a scintillation counter and interfaced to a PDP-15 computer was used to measure 2274 intensities (four octants) within a sphere of $2\theta \leq 100°$ with Cu Kα radiation (1.5418 Å). A θ-2θ scan technique was used with a β filter inserted (and counting time increased) only when K_β was calculated to make a contribution within the scan range. There was no significant crystal decomposition as judged by repeated measurements of three standard reflections. Correction for Lorentz-polarization effects and averaging of equivalent data yielded 884 observed reflections ($F_o \geq 3\sigma$). Estimated deviations in the structure factors were calculated by the finite difference method.[14] Owing to the almost spherical size of the crystal and the relatively limited variation of the transmission factor ($0.29 < T < 0.42$), no absorption corrections were made.

Routine application of MULTAN[15] yielded the positions of all the nonhydrogen atoms. These parameters were refined anisotropically using a full-matrix least-squares procedure[16] with hydrogen atoms included at calculated positions. A final conventional residual index, R, of 0.064 was obtained after some readjustment for overweighting reflections at either very high or very low values of $\sin \theta/\lambda$.[17] The corresponding R_w was 0.063. Fractional coordinates, thermal parameters, and observed and calculated structure factors are listed in the supplementary material; see paragraph at end of paper regarding supplementary material. A computer drawing[18] of the molecule is shown in Figure 1 and intramolecular bond distances and angles are given in Table I.

In the preparations and characterizations which follow, a nitrogen atmosphere was used to protect water- and/or air-sensitive substances.

1,4,7-Triazacyclononane. Although our route to the trihydrobromide of the title compound is based upon that described in the literature,[19-23] we find the following preparations of the intermediates more convenient.

Ditosylate of Ethylene Glycol.[19] Ethylene glycol (28 mL, 0.50 mol) in 100 mL of pyridine was added over a 2.5-h period to a stirred mixture of tosyl chloride (210 g, 1.10 mol) in 225 mL of pyridine. Some cooling with a cold water bath was required. After the mixture was stirred for several hours, it was shaken with ice water for about 10 min and filtered. The residue was washed with ether, dilute sulfuric acid, water, and finally ether; all wash liquids were ice cold. Drying by vacuum pumping was followed by recrystallization from boiling acetonitrile (mp 123.5-125.0 °C, lit.[19] 126-127 °C; yield 75%).

1,4,7-Tritosyl-1,4,7-triazaheptane. While the procedure of Koyama and Yoshino was followed,[20] the product was recrystallized from acetonitrile rather than a relatively very large volume of methanol (mp 174-175 °C, lit.[21] 173 °C; yield 68%).

1,4,7-Tritosyl-1,4,7-triazacyclononane.[20-23] An ethanol solution (150 mL) of sodium ethoxide (5.3 g, 0.23 mol) was added to a hot ethanol slurry of 1,4,7-tritosyl-1,4,7-triazaheptane (56.6 g, 0.100 mol). After removal of the ethanol by distillation under reduced pressure, a 0.2 M solution of ethylene glycol ditosylate (37.0 g, 0.10 mol) in dimethylformamide was added over a 3-h period to a stirred, 95-110 °C, 0.2 M solution of the product of the sodium ethoxide reaction in dimethylformamide. After 1 h of additional stirring at 100 °C, the mixture was cooled overnight and then concentrated by distillation under reduced pressure until precipitation began. The concentrate was poured into 1 L of vigorously stirred water and filtered. The residue was washed with water, dried by vacuum pumping, and recrystallized from boiling acetone (mp 217-220 °C, lit.[23] 222-223 °C; yield 65%).

1,4,7-Triazacyclononane Trihydrobromide.[20,22,23] A mixture of 240 mL of 47% hydrobromic acid, 135 mL of glacial acetic acid, and 1,4,7-tritosyl-1,4,7-triazacyclononane (21.8 g, 0.047 mol) was refluxed for about 24 h, concentrated by atmospheric distillation to about 20% of the original volume, and filtered. The trihydrobromide in the residue was extracted into water, recovered by evaporation of the solvent in vacuo and recrystallized from boiling dilute hydrobromic acid (mp 280-283 °C dec, lit.[23] 277-278 °C; yield 70%).

1,4,7-Triazacyclononane. The trihydrobromide of the title compound was stirred vigorously with an excess of sodium hydroxide beads in benzene for at least 24 h. The benzene filtrate and washings were evaporated by distillation below 30 °C under reduced pressure to give a white, deliquescent solid which readily sublimed at 40 °C (0.1 mm) (mp 54.5-57.5 °C; ^{1}H NMR ($CDCl_3$) δCH_2 2.82 s, δNH 2.25 s). The extraction with benzene was repeated several times to obtain essentially a quantitative yield of the cyclic triamine.

10-Phospha-1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (1). Approximately 0.04 M solutions of tris(dimethylamino)phosphine (8.8 mmol) and 1,4,7-triazacyclononane (8.4 mmol) in toluene were simultaneously added at equal rates over a 4-h period to an approximately equal volume of stirred, refluxing toluene. Evolution of Me_2NH began less than 15 min after starting the addition. Reflux was continued after termination of addition for at least 3 h, until a white precipitate was noted on the glass. Gas evolution had not ceased at this point, however. The reaction mixture was cooled and used to prepare the sulfide (**3**) and selenide (**4**) derivatives.

Efforts to isolate and characterize **1** were unsuccessful. Withdrawal of a portion of the reaction mixture supernatant led to rapid formation of a gel. Removal of the toluene by distillation below 30 °C under reduced pressure left a white, intractable solid. However, ^{31}P NMR resonances at 155 and 142 ppm were noted when the reaction was carried out in an NMR tube with rapid mixing of the reactants. Addition of sulfur to this reaction mixture gave chloroform-soluble products with ^{31}P shifts of 148 and 104 ppm, corresponding to **3** and an uncharacterized substance, respectively. Since the ratios of the two peaks were quite different after addition of the sulfur, an assignment of δ^{31}P for **1** could not be made.

10-Oxo-10-phospha-1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (2). Phosphorus oxychloride (1.19 g, 7.76 mmol) in 24 mL of benzene was added over a period of 1 h to an ice-cooled solution of 1,4,7-triazacyclononane (9.95 g, 7.70 mmol) and triethylamine (2.34 g, 23.2 mmol) in 50 mL of benzene. After stirring at room temperature for 2 h, the mixture was filtered under nitrogen and the residue washed with 200 mL of benzene. Evaporation of the solvent under reduced pressure gave a residue which upon recrystallization from boiling benzene/hexanes gave white crystals of product (mp 215 °C dec; 22% yield; *m/e* 173.0712 ± 0.001, calcd 173.0718 for $C_6H_{12}N_3PO$).

10-Thio-10-phospha-1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (**3**). A 5–10% excess of sublimed sulfur was added to a room temperature reaction mixture of **1**, which then was refluxed for 30 min. Evaporation of the solvent under vacuum followed by sublimination of the residue at 100 °C (0.1 mm) and crystallization of the sublimate from a freshly filtered chloroform solution by addition of at least ten volumes of ether gave **3** (mp 218.5–222.0 °C; 40% yield; *m/e* 189.0492 ± 0.001, calcd 189.0490 for $C_6H_{12}N_3PS$; ^{13}C NMR ($CDCl_3$) δCH_2 51.5 d, $^2J_{PC} = 7.9$ Hz).

10-Seleno-10-phospha-1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (**4**). A 1% excess of red selenium[24] was added to the room temperature reaction mixture of **1**, which then was refluxed for 90 min. Evaporation of the solvent under vacuum followed by sublimation of the residue at 100 °C (0.1 mm) and crystallization of the sublimate from a freshly filtered chloroform solution by addition of at least ten volumes of benzene gave **4** (mp 180 °C dec; yield 25%; *m/e* 236.9929 ± 0.001, calcd 236.9934 for $C_6H_{12}N_3PSe$; ^{13}C NMR ($CDCl_3$) δCH_2 51.6 d, $^2J_{PC} = 6.9$ Hz).

Titration of 3 with Diborane. The apparatus and general procedure have been described elsewhere.[25] Diborane was added in increments to a solution of **3** in methylene chloride. The pressure was measured after each diborane increment had been allowed to react for 20 min at dry ice/2-propanol slush bath temperature. A plot of system pressure vs. BH_3/**3** mole ratio revealed that reaction ceased at a 1.85:1 ratio. The crude product, insoluble in CH_2Cl_2, $CHCl_3$, and CH_3CN, gave three infrared bands in the B–H stretching region: 2377, 2317, and 2280 cm^{-1} (Nujol) and 2362, 2314, and 2266 cm^{-1} (dimethylformamide). In the latter solvent some gas evolution and formation of a milky emulsion occurred. The highest significant low-resolution mass spectral peak appeared at *m/e* 189 (**3**), but a very weak peak at the nominal molecular weight for **3**$\cdot 2BH_3$ was also present.

2-Dimethylamino-2-thio-1,3-dimethyl-1,3,2-diazaphospholane. An excess of anhydrous dimethylamine was bubbled into a stirred, ice-cooled 1,2-dichloroethane solution of 2-chloro-2-thio-1,3-dimethyl-1,3,2-diazaphospholane, prepared according to the procedure of Revel and Navech.[26] After 4 h of stirring at room temperature, the mixture was washed twice with ice-cold water and the organic layer dried with magnesium sulfate and concentrated to a yellow liquid (89% yield). Chromatography (silica gel/acetone) yielded a pale yellow liquid suitable for spectroscopic analyses (^1H NMR ($CDCl_3$) $\delta N(CH_3)_2$, δNCH_3 2.55 d, $^3J_{PH} = 11.8$ Hz, 2.80 d, $^3J_{PH} = 11.0$ Hz, δCH_2 2.08 m and 3.25 m; ^{13}C NMR ($CDCl_3$) δCH_2 46.9 d, $^2J_{PC} = 9.8$ Hz, δCH_3 36.3 d, $^2J_{PC} = 3.9$ Hz, δCH_3 20.6 d, $^2J_{PC} = 5.9$ Hz; ^{31}P NMR ($CDCl_3$) $\delta^{31}P$ 80 ± 0.5 s).

Tris(aziridinyl)phosphine. The procedure of Nuretdinov and Grechkin[27] was used and the crude yellow product was distilled at 80 °C (10 mm) (^1H NMR (C_6H_6) δCH_2 1.80 d, $^3J_{PH} = 8.8$ Hz; ^{13}C NMR (C_6H_6) δCH_2 21.4 d, $^2J_{PC} = 4.9$ Hz).

Caution. Distillation led to an explosion when the oil bath temperature reached about 120 °C and the pot residue began to thicken.

Tris(aziridinyl)phosphineborane. A 1 M tetrahydrofuran solution of $H_3B\cdot THF$ was added to an equimolar amount of tris(aziridinyl)phosphine in the same solvent. Evaporation of the solvent produced the product which was recrystallized from benzene/petroleum ether (mp 45.0–45.5 °C; ^1H NMR (C_6H_6) δCH_2 1.97 d, $^3J_{PH} = 12.8$ Hz, $\delta^{11}BH_3$ 0.65 qd, $^1J_{^{11}BH} = 96$, $^2J_{P^{11}B} = 16 \pm 1$ Hz; ^{13}C NMR (C_6H_6) δCH_2 23.0 d, $^2J_{PC} = 4.0$ Hz).

Tris(aziridinyl)phosphine Sulfide. The procedure of Nuretdinov and Grechkin[27] gave this compound, which was recrystallized from benzene/petroleum ether (mp 53–54 °C; lit.[28] 53–54 °C; ^1H NMR (C_6H_6) δCH_2 1.82 d, $^3J_{PH} = 16.6$ Hz; ^{13}C NMR (C_6H_6) δCH_2 23.3 d, $^2J_{PC} = 6.9 \pm 0.5$ Hz).

Tris(aziridinyl)phosphine Selenide. Red selenium[24] and tris(aziridinyl)phosphine reacted completely in less than 1 h at room temperature to give a white solid which was recrystallized from benzene/petroleum ether (mp 74–75 °C; ^1H NMR (C_6H_6) δCH_2 1.80 d, $^3J_{PH} = 17.0$ Hz; ^{13}C NMR (C_6H_6) δCH_2 23.8 d, $^2J_{PC} = 5.9$ Hz).

Discussion

In contrast to the behavior of $P(NMe_2)_3$ and **5**, **1** is unstable with respect to formation of a polymer-like material. The instability of **1** made in a manner similar to ours was noted in a recent brief communication.[22] Compound **1** does not form detectable quantities of **2** when solutions of **1** are subjected to a variety of oxidizing agents. The oxide **2** can be made by condensing $OPCl_3$ with the cyclic triamine, however. By contrast, oxidation of **1** with sulfur and selenium is facile, giving **3** and **4**, respectively, as is the case with $P(NMe_2)_3$ and **5**.[8] However, unlike the oxide and sulfide of $P(NMe_2)_3$ and of **5**, compounds **2** and **3** decompose slowly in the solid state and more rapidly in organic solvents. Adventitious water may be hydrolyzing **2** and **3** which, as will be shown in the case of **3**, contain strained five-membered rings. A further contrast in the present structures is their behavior toward BH_3. Whereas $H_3BP(NMe_2)_3$, **9**, and **10** are stable adducts,[8] attempts to form a BH_3 adduct of **1** sufficiently stable for isolation have failed. The consequences of constraint in the sulfide derivatives **7** and **3** are also apparent from tensimetric titrations of these compounds and $SP(NMe_2)_3$ with B_2H_6. No adduct is detected with $SP(NMe_2)_3$[8,9] while **7** forms the mono adduct **11**[8,9] and **3** forms a diadduct. The latter adduct exhibits only a parent ion peak for **3** under a variety of mass spectral conditions. Infrared and NMR analysis of the diadduct leave ambiguous whether the BH_3 groups link to two nitrogens or to a nitrogen and the sulfur. In either case, these results are consistent with distortion of the nitrogen bond angles in **7** and **3** which lowers the nitrogen reorganization energy required for adduct formation.[29]

The ease of BH_3 diadduct formation of **3** in addition to the reasons stated in the Introduction prompted us to carry out a determination of the crystal and molecular structure of **3** by X-ray means. From the structure shown in Figure 1 and the structural parameters given in Table I, it is seen that, despite the considerable tendency for nitrogen to adopt a planar coordination geometry in PNR_2 systems,[2] the nitrogens in **3** are pyramidal with average bond angles of 109°. By contrast, the NPN angles (101° av) remain near those encountered in isomeric $SP(\overline{NCH_2CH_2})_3$ (100°).[30] This observation extends the scope of the "hinge effect", proposed earlier by one of us for $OP(OR)_3$ systems,[31] to $ZP(NR_2)_3$ compounds. In this effect the POC angles (here PNC) which prefer to be near 120° are found to flex in preference to the OPO angles (here NPN) when the molecule is constrained into a symmetrical polycyclic structure. Each of the five-membered rings contains a carbon atom (C2, C4, and C6 in Figure 1) which is puckered toward the sulfur and out of the nearly planar arrays of the remaining ring atoms. The effect of this puckering is to create an average dihedral angle of 11.6° in the S–P–N–lp system. The structure of **3** implies that **1** undoubtedly also contains pyramidal nitrogens.[32] Although the structure of **1** probably has C_{3v} symmetry (or nearly so), it is not possible to infer from this any conclusions concerning a postulated C_{3v} conformation of $P(NMe_2)_3$[7] since the nitrogen coordination geometries are undoubtedly not the same.

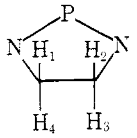
From the structural data available for **3** and $SP(\overline{NCH_2CH_2})_3$, it is possible to account for most of the differences in the behaviors toward BH_3 of the tris(dialkylamino)phosphorus systems under discussion. The sum of the angles around nitrogen in **3** is 327° whereas that in $SP(\overline{NCH_2CH_2})_3$ is 338°, which implies that the greater p character of the nitrogen lone pairs in the latter permits better π donation to the phosphorus. Such an inductive effect could increase the phosphorus basicity, permitting isolation of stable $H_3BP(\overline{NCH_2CH_2})_3$ but not the borane adduct of **1**. The shorter PN distance in $SP(\overline{NCH_2CH_2})_3$[30] (1.64 Å) compared to **3** (1.68 Å) is not inconsistent with this notion. If this reasoning can also be applied to $P(\overline{NCH_2CH_2})_3$ and **1**, then the greater p character of the nitrogen lone pair in $P(\overline{NCH_2CH_2})_3$ would allow a stronger orbital interaction with the phosphorus lone pair. This favors a greater phosphorus Lewis basicity and hence a more stable BH_3 adduct.[33] These relative perturbations

Table II. ^{31}P NMR Chemical Shifts for XP(N<) Compounds[a]

parent phosphine	X: O	S	Se	lp	BH_3
$P(NMeCH_2)_3CMe$ (**5**)[b]	19	73	78 (854)[c,d]	84	89
$Me_2NPNMeCH_2CH_2NMe$	26[e]	80		114[e]	
$P(NMe_2)_3$[b]	25	82	83 (784)[c,d]	122	105
$P(NCH_2CH_2)_3$[f]	41	117	133 (851)[c]	129	127
1	99	148	146 (890)[c]	142[g] or 155	

[a] Because of the different sources of the $\delta^{31}P$ values and the different solvents used, the numbers were rounded off to the nearest whole number even though precisions to ±0.1 ppm are quoted. [b] $\delta^{31}P$ values measured in $CHCl_3$: Kroshefsky, R. D.; Verkade, J. G. *Phosphorus Sulfur*, in press. [c] $^1J_{PSe}$ coupling value. [d] Taken from ref 35. [e] $\delta^{31}P$ values from Mavel, G. *Annu. Rep. NMR Spectrosc.* **1973,** *5B*. [f] Measured in C_6H_6. [g] Compound could not be purified (see text).

Table III. Results of LAOCN III Analyses of ^1H NMR Spectra[a,b]



	ν_1, ν_2	ν_3, ν_4	$^3J_{H_1P}$ $^3J_{H_2P}$	$^3J_{H_3P}$ $^3J_{H_4P}$	$^3J_{H_1H_2}$	$^3J_{H_3H_4}$	$^2J_{H_1H_4}$[b] $^2J_{H_2H_3}$	$^3J_{H_1H_3}$[b] $^3J_{H_2H_4}$
2	3.19	3.55	11.8	10.2	6.0	6.0	−12.0	6.3
3	3.25	3.63	13.1	11.7	6.1	6.0	−12.2	6.4
4	3.21	3.62	13.4	12.2	6.2	6.2	−12.2	6.3
$Me_2N(S)PNMeCH_2CH_2NMe$	3.08	3.25	7.3	13.0	7.5	7.5	− 8.5	5.7

[a] Spectra obtained at 100 MHz on $CDCl_3$ solutions. Values of δ and J are in parts per million and hertz, respectively. The root mean square errors range from 0.15 to 0.18. At least 77% of the 48 calculated ^1H transitions were assigned in each case. Assignments not made were due to lack of peak resolution or to weak intensity. [b] Although interchange of these geminal and vicinal couplings causes no change in any of the NMR spectra, the assignments given are considered correct since HCH geminal couplings have been shown to be generally negative (Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Elmsford, N.Y., 1969; pp 270–277.

are predicated on the assumption that the nitrogen lone pairs in the conformationally nonrigid $H_3BP(NCH_2CH_2)_3$ are able to achieve a nearly eclipsed relationship with the P–B axis as effectively as in the rigid borane adduct of **1**.[34]

The ^{31}P NMR data in Table II show two interesting features. A distinct shift to lower field is generally encountered for $XP(NCH_2CH_2)_3$ and **1–4** compared to the remaining three systems. This phenomenon may be associated with the presence of pyramidal nitrogens in the former two series. The second feature is the large magnitude of the $^1J_{PSe}$ couplings for all the selenides recorded except for $SeP(NMe_2)_3$. Elsewhere we have reported a strong correlation between this parameter and the BH stretching frequencies of the corresponding BH_3 adducts for a series of acyclic, cyclic, and bicyclic phosphite esters.[35] Since νBH is a function of phosphite Lewis basicity[9] and $^1J_{PSe}$ increases with poorer basicity,[35] it may be concluded that **1** contains the poorest phosphorus base. This conclusion is consistent with our inability to form a stable BH_3 adduct of **1**. According to the $^1J_{PSe}$ trend in Table II, the order in phosphorus basicity should be $P(NMe_2)_3$ > $P(NCH_2CH_2)_3$ > $P(NMe_2CH_2)_3CMe$ > **1**. This order is also corroborated by the trend in the weighted averages of the symmetric and asymmetric stretches[9] of the borane adducts of the first three members of this series measured in CCl_4 (2359, 2368, and 2381 cm^{-1}, respectively).

The ^1H NMR spectra of **2–4** are complex, giving rise to 20–30 absorptions in a roughly mirror image pattern. The $CDCl_3$ spectra of these compounds and that of $Me_2N(S)PNMeCH_2CH_2NMe$, the monocyclic analogue of **3**, were analyzed as the AA'BB' portions of AA'BB'X spin systems at 60 and 100 MHz.[36] The rise in $^3J_{PH}$ in Table III from oxide to sulfide to selenide is typical for chalconides of $P(NMeCH_2)_3CMe$ (**5**),[8,33] $P(NMe_2)_3$,[37] and $P(NCH_2CH_2)_3$ (see Experimental Section). Unusual, however, is the significantly smaller value for $^2J_{H_1H_4}$ = $^2J_{H_2H_3}$ for **3** compared to $Me_2N(S)P(NMeCH_2CH_2NMe)$ as well as other 1,3-dimethyl-1,3,2-diazaphospholanes.[38,39] Others[40] have noted that geminal proton couplings for a methylene group α to nitrogen range unusually widely, even in apparently related structures. Although no structural data are available on a monocycle such as $Me_2N(S)PNMeCH_2CH_2NMe$,[41] it is probable that the nitrogens are planar in contrast to the pyramidal nitrogens found for **3** in the present work, thus providing a rationale for the disparate geminal couplings.

Unlike $SP(NCH_2CH_2)_3$ (NSC 06396), which is quite active against leukemia 1210 tumors in mice, its isomer **3** is inactive. It is reasonable to suppose that the weaker alkylating properties of the latter derive from less strain in the larger rings.

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Supplementary Material Available: Fractional coordinates, thermal parameters, observed and calculated structure factors, and a computer drawing of the unit cell (6 pages). Ordering information is given on any current masthead page.

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An Unusual Twist-Boat Conformation for a Six-Membered Ring Phosphorus Heterocycle

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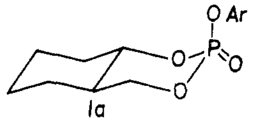
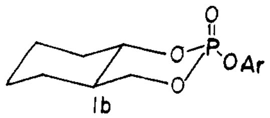
Abstract: Configurational and conformational analysis of isomeric 2-*p*-nitrophenoxy-2-oxo-1,3,2-dioxaphosphorinane (**1**) and isomeric 2-*p*-nitrophenoxy-2-oxo-1,3,2-oxazaphosphorinane (**2**) is presented. Based upon ^{1}H NMR coupling data and ^{31}P NMR spectra the axial and equatorial *p*-nitrophenoxy isomers of **1** are both in chair conformations as is the axial isomer of **2**. However, NMR data support the assignment of a twist-boat conformation for the equatorial isomer of **2**.

Introduction

Recent work has established that an electronegative substituent on phosphorus in a 2-oxo-1,3,2-dioxaphosphorinane **1** prefers the axial orientation.[2-11] This result is consistent with molecular orbital calculations associated with the generalized anomeric or gauche effect.[12,13] Generally, the magnitude of this anomeric effect at phosphorus is small (less than several kcal/mol) and both axial and equatorial isomers of **1** are in the chair conformation. In the present paper NMR analysis of the conformation of both the axial and equatorial 2-*p*-nitrophenoxy esters of the 2-oxo-1,3,2-dioxaphosphoranes, **1,** confirms this conclusion. In contrast NMR analysis of the equatorial isomer of 2-oxo-1,3,2-oxazaphosphorinane **2b** shows it to be in an unusual twist-boat conformation.



1a



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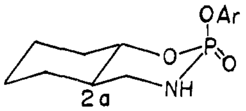

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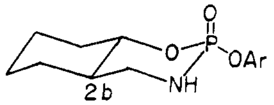
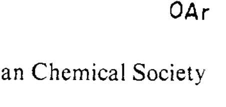


2b



2c

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