Registry No. 1 ($R_1 = R_2 = NH_2$), 91759-18-1; 1 ($R_1 = R_2 =$ NHMe), 91759-21-6; 1 ($R_1 = R_2 = NHSiH_3$), 91759-22-7; 1 ($R_1 = R_2 = N(SiH_3)_2$), 91759-23-8; 2 ($R_1 = R_2 = NH_2$), 91759-19-2; 2 ($R_1 = R_2 =$ NHMe), 91759-26-1; 2 ($R_1 = R_2 = NHSiH_3$), 91759-27-2; 3 ($R_1 = R_2 = NH_2$), 91759-20-5; 3 ($R_1 = R_2 =$ NHMe), 91759-24-9; 3 ($R_1 = R_2 = NHSiH_3$), 91759-25-0; 4 (R = H), 91759-28-3; 4 ($R = NO_2$), 91759-29-4; *trans*-1,3-butadiene, 106-99-0; *trans*-1,3-butadiene dianion, 63365-91-3.

Contribution from the Department of Chemistry and Ames Laboratory—DOE, Iowa State University, Ames, Iowa 50011,
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Stereoelectronic Effects of Cyclization in Aminophosphine Systems: Structural, PES, and NMR Study of $Me_2NP(OCH_2)_2CMe_2$ and $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$

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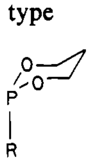
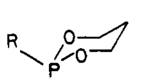
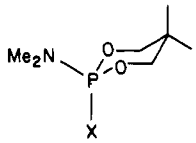
X-ray diffraction and NMR and PE spectral evidence is presented for equatorial R_2N groups in the solid, solution, and gas phases of the title 1,3,2-dioxaphosphorinanes (1 and 2, respectively). This contrasts with the behavior of MeO-substituted analogues wherein the MeO substituent strongly prefers the axial position:[5b] In the solid state, 1 ($a = 6.542$ (1) Å, $b = 11.731$ (3) Å, $c = 6.440$ (2) Å, $\alpha = 101.53$ (4)°, $\beta = 83.52$ (3)°, $\gamma = 90.96$ (3)°, triclinic, $Z = 2$) and 2 ($a = 8.464$ (1) Å, $b = 9.868$ (2) Å, $c = 27.832$ (2) Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, *Pbna*, $Z = 8$) display a planar stereochemistry about the nitrogen with the plane nearly containing the P–lone pair axis. The structural parameters are also consistent with substantial $N \rightarrow P\ \pi$ bonding. Perhaps because of overlap of the IE_N and IE_p lone-pair bands in 1, 2, and $Me_2NP(OCH_2)_2CH_2$ (7),[23] the conclusion based on a rough comparison of the IE_p data that these compounds are more basic than $Me_2NP(OMe)_2$[21a] is rendered tentative. Support for this conclusion can, however, be found in a comparison of ${}^1J_{PSe}$ values for $Me_2NP(OMe)_2$ and a conformationally rigid selenide analogue of 1. The validity of comparing trends in IE_p data on classes of trivalent phosphorus compounds with those in ${}^1J_{PSe}$ values of their selenide derivatives is verified by showing that these parameters yield a linear correlation in the case of phosphite esters and their selenophosphate derivatives.

Introduction

The molecular structures of aminophosphorus compounds continue to be interesting because of the variety of bond angles around nitrogen that they display,[2] the controversies regarding the preferred conformation of the NR_2 groups in molecules such as $P(NMe_2)_3$[2] and $R_2N\overline{PNMeCH_2CH_2N}Me$,[3] and the influences of these stereochemical effects on electronic properties such as the basicity of phosphorus.[2,4] Owing to a lack of crystallinity, solid-state structural information on aminophosphorus compounds in which phosphorus is trivalent is currently small compared to that for cognates which incorporate four-coordinate phosphorus. Constraints imposed on P(III) substituents that are linked to form five-or six-membered rings generally lead to substantial changes in phosphorus basicity.[5] Moreover, the exocyclic group in six-membered ring systems of the type may adopt the axial position for electronic reasons or the equatorial location for primarily steric causes[6,7] The above considerations and the observation that 1 and 2 are crystalline led us to investigate the molecular structures of these compounds by X-ray diffraction, their photoelectron spectral properties, and the ${}^1J_{PSe}$ spin–spin couplings of their corresponding selenides 1a and 2a. We present evidence that both 1 and 2 prefer the conformations shown in the solid, solution, and gaseous states, that the nitrogens are nearly planar in the solid state, and that the phosphorus atoms in the solution and gas phases are more basic than that of the acyclic analogue $Me_2NP(OMe)_2$. Of aid in these studies were the ${}^{31}P$ NMR spectra of the conformationally rigid 3 and 4[8] and their selenide derivatives 3a and 4a, which served as model compounds for comparison.







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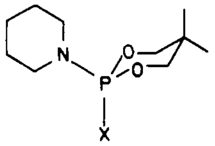
1a: X = Se



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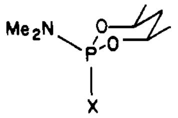
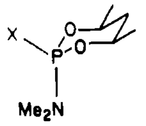


3: X = lone pair
3a: X = Se



4: X = lone pair
4a: X = Se

Experimental Section

Preparations. Compound 1 and 2 were prepared by following a previous report[9] and were purified by repeated sublimation under

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(1) (a) Department of Chemistry, Iowa State University. (b) Ames Laboratory—DOE, Iowa State University. (c) Department of Chemistry, University of Texas at Austin.

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vacuum (0.1 torr) at room temperature and 60 °C, respectively (^{13}C NMR (δ, $(CD_3)_2CO/CF_2Cl_2$) 21.3 s (CCH_3 (ax)), 22.9 s (CCH_3 (eq)), 33.0 s (C_4C), 35.0 d (C_2N, $^2J_{PC}$ = 22), 73.8 s (CO)). Selenation of **1a** and **2a** was carried out by following a procedure described previously.[4] Conversion of $Me_2NP(OMe)_2$ to $Me_2N(Se)P(OMe)_2$ was accomplished by the same method.[4] The product isolated upon workup of the reaction mixture was of sufficient purity as judged by its ^{1}H and ^{31}P NMR spectra that further purification by distillation of this thermally unstable material was not carried out. Reaction of $(MeO)_2PCl$ with Me_2NH gave $(MeO)_2PNMe_2$ with use of the method employed to prepare **1** and **2**.[8] Purity was established by comparing its ^{1}H and ^{31}P NMR spectra to those reported previously for this compound.[11]

A mixture of compounds **3** and **4** was made as described earlier.[8] The ratio of **3** to **4** was approximately 3:2 (as judged by ^{1}H and ^{31}P NMR spectroscopy) instead of 10:1 as reported previously with these NMR techniques. When the mixture was heated at 135 °C for 2 h, no change in this ratio occurred. Addition of a catalytic amount of *p*-toluenesulfonic acid did produce an approximately 9:1 ratio after 22 h at 25 °C. Selenation of the 3:2 and 9:1 mixtures of **3** to **4** was carried out by the procedure described earlier,[4] and the reaction mixtures were examined by ^{31}P NMR spectroscopy (see text).

Crystals of **1** and **2** suitable for X-ray diffraction were grown by sealing approximately 0.05 g of each compound in an evacuated (~0.1 torr) 10 cm long glass tube (10 mm o.d.). The bottom of the tube was placed in a sand bath and slowly heated. Compounds **1** and **2** sublimed at 27 and 55 °C, respectively. Due to the low melting point of compound **1** (28 °C), it was necessary to select and mount crystals in a cold room, which was maintained at 14 °C. A colorless crystal of **1** in the form of a parallelepiped (0.3 × 0.4 × 0.2 mm) was mounted in a Lindemann capillary that was sealed to prevent hydrolysis by atmospheric moisture. The crystal was found to be triclinic with a = 6.542 (1) Å, b = 11.731 (3) Å, c = 6.440 (2) Å, α = 101.53 (4)°, δ = 83.52 (3)°, γ = 90.96 (3)°, μ = 2.45 cm^{-1}, Z = 2, and a density of 1.22 g/cm^3, which was computed on a cell volume of V = 481.1 (2) Å^3. A Howells, Phillips, and Rodgers plot[12] indicated a centrosymmetric lattice which led unambiguously to the space group $P\bar{1}$. This space group was confirmed by subsequent solution and refinement of the structure. The data are collected at −130 ± 3° on a Syntex P2$_1$ diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.709 65 Å) employing a ω-scan procedure. Low-temperature data were collected in order to minimize thermal motion. Data from the four octants hKl, $hK\bar{l}$, $h\bar{K}l$, and $\bar{h}Kl$ were collected within a sphere of $2\theta < 50°$, yielding 2645 measured intensities. there was no significant crystal decomposition as judged by repeated measurements of three standard reflections. Averaging of equivalent data yield 1220 observed reflections ($F_o \geq 3\sigma(F_o)$). Lattice constants were obtained by a least-squares refinement of the $\pm 2\theta$ ($|2\theta| > 20°$) measurements of 24 standard reflections. The structure was solved by standard heavy-atom procedures following location of the phosphorus atom from the Patterson map and refinement by block-matrix least-squares methods. Fourier-difference maps and least-squares refinement led to location of all non-hydrogen atoms. Isotropic refinements of these positions gave a conventional R factor of 0.19 and a weighted R of 0.265. Subsequent anisotropic refinement yielded a conventional R factor of 0.114 and a weighted R of 0.172. Ring hydrogen positions were then calculated, and full-matrix least-squares refinement led to a final conventional R of 0.074 and a weighted R of 0.121. The scattering factors[13a] for the phosphorus atom were modified to account for anomalous dispersion effects.[13b]

Table I. Bond Distances (Å) and Angles (deg) for $Me_2NP(OCH_2)_2CMe_2$ (**1**)

P-O1	1.640 (4)	N-C2	1.469 (9)
P-O2	1.652 (4)	C3-C5	1.525 (7)
P-N	1.642 (5)	C4-C5	1.532 (8)
O1-C3	1.452 (7)	C5-C6	1.549 (9)
O2-C4	1.453 (7)	C6-C7	1.547 (7)
N-C1	1.447 (7)		
N-P-O1	99.23 (22)	O1-C3-C5	111.80 (38)
N-P-O2	101.50 (22)	O2-C4-C5	109.92 (34)
O1-P-O2	97.73 (20)	C3-C5-C4	108.80 (30)
C1-N-C2	115.12 (49)	C3-C5-C6	108.08 (40)
C1-N-P	125.30 (45)	C3-C5-C7	111.83 (36)
C2-N-P	119.58 (37)	C4-C5-C6	108.11 (37)
P-O1-C3	114.75 (24)	C4-C5-C7	109.99 (35)
P-O2-C4	112.32 (29)	C6-C5-C7	110.63 (35)

Table II. Bond Distances (Å) and Angles (deg) for $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$ (**2**)

P-O1	1.675 (16)	C4-C5	1.556 (43)
P-O2	1.623 (18)	C5-C6	1.536 (21)
P-N	1.637 (12)	C5-C7	1.556 (20)
O1-C3	1.461 (32)	C1-C3N	1.582 (28)
O2-C4	1.426 (33)	C2-C4N	1.521 (30)
N-C1	1.505 (22)	C3N-C5N	1.501 (26)
N-C2	1.502 (21)	C4N-C5N	1.632 (27)
C3-C5	1.515 (44)		
O1-P-O2	97.39 (79)	C3-C5-C6	110.61 (222)
N-P-O1	100.61 (93)	C3-C5-C7	109.65 (228)
N-P-O2	100.18 (90)	C4-C5-C6	110.00 (238)
C1-N-P	120.88 (95)	C4-C5-C7	111.82 (74)
C2-N-P	124.33 (106)	C6-C5-C7	107.53 (119)
C1-N-C2	114.25 (118)	N-C7-C3N	108.04 (161)
P-O1-C3	115.87 (140)	C1-C3N-C5N	112.22 (151)
P-O2-C4	114.77 (137)	C3N-C5N-C4N	106.27 (143)
O1-C3-C5	112.18 (188)	C5N-C4N-C2	110.13 (153)
O2-C4-C5	112.76 (186)	C4N-C2-N	109.55 (173)

Table III. Final Positional Parameters for $Me_2NP(OCH_2)_2CMe_2$ (**1**)

	x	y	z
P	0.0858 (2)	0.2816 (1)	−0.0080 (2)
O1	0.1347 (5)	0.2862 (3)	0.7382 (6)
O2	0.8443 (5)	0.2385 (3)	0.9884 (6)
N	0.2044 (7)	0.1593 (4)	0.9917 (8)
C1	0.2081 (10)	0.0559 (5)	0.8250 (11)
C2	0.3179 (9)	0.1496 (6)	0.1718 (11)
C3	0.0011 (8)	0.3625 (4)	0.6617 (8)
C4	0.7134 (8)	0.3200 (5)	0.9214 (9)
C5	0.7770 (7)	0.3247 (4)	0.6869 (8)
C6	0.6428 (9)	0.4184 (5)	0.6277 (10)
C7	0.7458 (9)	0.2044 (5)	0.5442 (9)
H1A	−0.0889	0.4281	0.7654
H1B	−0.0681	0.3363	0.5204
H2A	0.7278	0.4031	1.0200
H2B	0.5597	0.2929	0.9398

The crystal and molecular structure of compound **2** was determined with use of the same methodology as for **1**. The pyramidal crystal (0.4 × 0.2 × 0.2 mm) was found to be orthorhombic (at 21 °C) with a = 8.464 (1) Å, b = 9.868 (2) Å, c = 27.832 (2) Å, μ = 1.70 cm^{-1}, Z = 8, and a volume of 2323.9 Å^3 with a calculated density of 1.24 g/cm^3. Systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $h + 1 = 2n + 1$; $0kl$, $k = 2n + 1$; $kh0$, $h = 2n + 1$; $00l$, $l = 2n + 1$ indicated the space group $Pbna$, which was confirmed by solution of the structure. Data were collected on a four-circle diffractometer designed and built in the Ames Laboratory, equipped with a scintillation counter and interfaced to a PDP-15 computer. With use of graphite-monochromated Mo Kα radiation, 1465 reflections in the two octants hKl and $\bar{h}Kl$ were observed within a sphere of $2\theta < 50°$. No decomposition of the crystal was observed upon monitoring three standard reflections. Averaging of equivalent data yielded 560 independent reflections ($F_o > 3\sigma(F_o)$). Block-matrix least-squares refinement of the positions and anisotropic thermal parameters for all non-hydrogen atoms yielded a conventional R of 0.103 and a weighted R of 0.141. Hydrogen positions were calculated, and a final full-matrix anisotropic refinement of the non-hydrogen positions led to a final conventional R of 0.084 and a weighted R of 0.117. Tables I and II list the bond lengths and bond angles for **1** and **2**, respectively, and Tables III and IV contain

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Table IV. Final Positional Parameters for $CH_2(CH_2CH_2)_2NP(OCH_2)_2CMe_2$ (2)

	x	*y*	*z*
P	0.7472 (10)	0.1762 (3)	0.0892 (1)
O1	0.5972 (15)	0.2863 (15)	0.0932 (4)
O2	0.8897 (10)	0.2834 (15)	0.0997 (3)
N	0.7355 (27)	0.1019 (13)	0.1417 (4)
C1	0.7189 (31)	0.9509 (17)	0.1458 (5)
C2	0.7156 (28)	0.1738 (18)	0.1884 (6)
C3	0.6058 (29)	0.4026 (27)	0.0615 (7)
C4	0.8967 (27)	0.3957 (27)	0.0670 (8)
C5	0.7503 (40)	0.4895 (14)	0.0710 (5)
C6	0.7641 (39)	0.6043 (16)	0.0338 (5)
C7	0.7385 (29)	0.5567 (15)	0.1214 (5)
C3N	0.8435 (21)	0.8985 (21)	0.1838 (6)
C4N	0.8394 (24)	0.1263 (20)	0.2240 (6)
C5N	0.8203 (20)	0.9624 (18)	0.2322 (6)
H3A	0.4962	0.4596	0.0656
H3B	0.5996	0.3654	0.0244
H4A	0.9970	0.4601	0.0761
H4B	0.9108	0.3650	0.0371
H1A	0.6171	1.000	0.1581
H1B	0.7611	1.000	0.1148
H2A	0.7281	0.2795	0.1839
H2B	0.5995	0.1561	0.2028
H3NA	0.9593	0.9221	0.1710
H3NB	0.8330	0.7946	0.1875
H4NA	0.8006	0.0688	0.2557
H4NB	0.9410	0.0744	0.2115
H5NA	0.7123	1.019	0.2397
H5NB	0.9126	1.200	0.2489

their respective fractional atomic positions. Anisotropic thermal parameters and structure factors are listed in the supplementary material; see paragraph at the end of this paper regarding supplementary material.

PES data were recorded as described earlier.[2a] ^{31}P, ^{13}C, and ^{1}H NMR data were obtained with a Bruker WM-300 FT-NMR spectrometer locked on the ^{2}H resonance of the deurated solvent. The external standard for the ^{31}P NMR spectra was 85% H_3PO_4, sealed in a 1 mm i.d. tube held coaxially in a 10-mm NMR sample tube by a PTFE vortex plug.

Results and Discussion

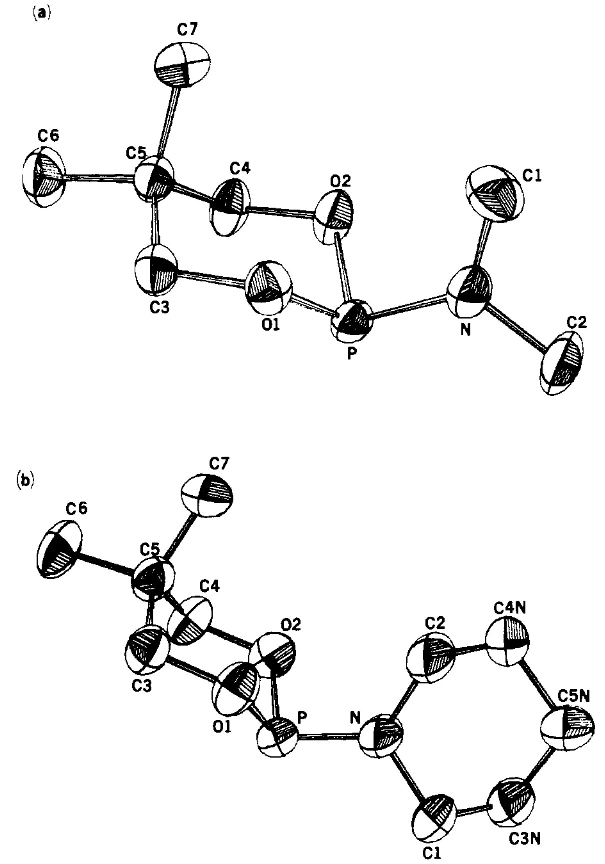
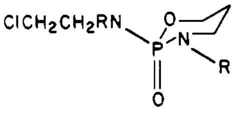


Figure 1. ORTEP drawings of (a) **1** and (b) **2**.

From the ORTEP drawings in Figure 1 it is seen that the phosphorinane ring in both **1** and **2** adopts a chair conformation. There is substantial solid-state evidence that, given a choice, dialkylamino groups generally occupy the equatorial position in 1,3,2-dioxaphosphorinane and 1,3,2-oxa-aza ring systems when the phosphorus is tetracoordinate and feature a nearly planar configuration about the nitrogen.[14] The present X-ray diffraction studies provide the first indication that these characteristics persist in the dioxaphosphorinanes when the phosphorus is trivalent. The planar stereochemistry of the nitrogen found in the solid state for many aminophosphorus compounds wherein phosphorus is tri- or tetracoordinate can be attributed to the presence of electronegative phosphorus substituents (such as oxygens in **1**, **2**, and **5**[14] or halogens as in R_2NPX_2[15]) which may serve to enhance π bonding from N to P. On the other hand, compounds such as $SeP[N(CH_2CH_2)_2CH_2]_3$[16] and $P[N(CH_2CH_2)_2CH_2]_3$[17] contain two nearly planar nitrogens while the third displays substantial pyramidal character. Here it might be argued that the presence of three electron-donating R_2N groups renders phosphorus insufficiently electronegative to maintain planarity of all three nitrogens. With two oxygens in the phosphorinane rings of **1** and **2** there is apparently sufficient phosphorus substituent electronegativity to induce nitrogen planarity in **1** (angle sum around N 360.0°) and in **2** (angle sum around N 359.5°). In the case of the acyclic aminophosphine Me_2NPF_2, a discrepancy exists between the X-ray crystal structure (angle sum around N 360.0°) and the gas-phase electron diffraction result (angle sum around N 348.4°).[18] It is interesting that the drive toward planarity of the nitrogen stereochemistry is sufficient to overcome the puckering tendency of the piperidine ring in **2** and also in two of these rings in $SeP[N(CH_2CH_2)_2CH_2]_3$[16] and $P[N(CH_2CH_2)_2CH_2]_3$.[17] The same is also true of two of the morpholino rings in $SeP[N(CH_2CH_2)_2O]_3$[16] and $P[N(CH_2CH_2)_2O]_3$.[17] It appears, however, that the piperidine ring in **2** accommodates nitrogen planarity mainly by opening the C1–N–C2 angle from the tetrahedral angle to about 114° and by flattening the C1–N–C2 plane with respect to the C1–C3N–C4N–C2 plane so that the acute angle between these two planes is approximately 53° instead of the 60° required for a cyclohexane chair conformation with tetrahedral bond angles. The reason for the excessively long C4N–C5N bond in **2** (1.632 Å) is not clear since the anisotropic thermal parameters for these atoms are not unusual nor are there unreasonably close intermolecular contacts.



5: $R = ClCH_2CH_2$, $R' = H$;
$R = H$, $R' = ClCH_2CH_2$;
$R = R' = ClCH_2CH_2$

Typical of R_2NPX_2[15,19] and $R_2NP(O)X_2$ (X_2 = OCCO or OCCNR ring systems[14]) is the proclivity of the C_2NP plane

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(19) See, for example: (a) Fonti, P.; Damiania, D.; Favero, P. G. *J. Am. Chem. Soc.* **1973**, *95*, 756. (b) Brittain, A. H.; Smith, J. E.; Lee, P. L.; Cohn, K.; Schwendeman, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 6772.

Table V. Ionization Energies[a]

	IE_N	IE_P	IE_O
$P(OMe)_3$[b]		9.22	10.54, 11.11, 11.3
$Me_2NP(OMe)_2$[c]	8.63	8.93	10.56 (a',a''), 11.01 (n_σ)
1[d]	8.95	8.95	9.80 (a',a''), 11.30 (n_σ)
2[d]	8.56	8.56	9.60 (a',a''), 11.30 (n_σ)
7[e]	8.70	8.70	10.0, 11.26
$(Me_2N)_2POMe$[c]	7.80 (a''), 9.15 (a')	8.59	10.63
$P(NMe_2)_3$[f]	7.89 (a''), 8.77 (a') 9.90 (a')	7.58	

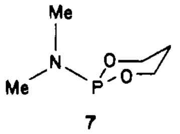
[a] In eV; "lone pair" energies unless stated otherwise. [b] Reference 22. [c] Reference 21a. [d] This work. [e] Reference 23. [f] Reference 2.

to be nearly perpendicular to the PX_2 plane. The same conformational property is seen in **1** and **2** wherein the C_2N planes are rotated from perpendicularity to the PO_2 plane by 2.2 and 1.9°, respectively. This result is consistent with the notion that the nitrogen and phosphorus lone pairs avoid repulsion and that the nitrogen lone pair enhances its tendency to π bond with phosphorus by adopting the observed conformation. Rotation of the P–N bonds in these compounds is apparently facile since the ^{13}C NMR spectrum of **1** shows no perceptible changes down to −84 °C in $(CD_3)_2CO/CF_2Cl_2$.

The P–N bonds in **1** and **2** (1.642 (5) and 1.631 (1) Å, respectively) are typical of those observed for several P(III)–N compounds,[20] a result that is consistent with the presence of π bonding in the P–N bond. Further evidence for enhanced P–N π bonding in **1** and **2** can be construed to emanate from their P–O–C angles, which averages 113.5 and 115.3°, respectively. These angles are distinctly smaller than the POC angles in the rings of **6**, which average 119.9°. This is consonant with the idea that the hybridization around the oxygens in **1** and **2** is closer to sp^3 whereas in **6** it is nearer to sp^2. The exocyclic POC angle in **6** (117.80°) is also larger than the POC angles in **1** and **2**. The results are consistent with the notion that the R_2N substituent is more capable of N–P π bonding than a methoxy group. This postulate is also supported by the slightly longer average P–O bond distances in **1** and **2** (1.646 (4) and 1.649 (4) Å, respectively) compared with that in **6** (1.617 (5) Å). A consequence of the larger POC angle in **6** is that the esteratic portion of each chair is more flattened than in **1** and **2**. Thus the acute angles between the planes made by the O1–P–O2 and O1–O2–C3–C4 portions of the ring in **1** and **2** are 74.1 and 76.5°, respectively. This compares with the corresponding angle of 36.9° in **6**. The sum of the angles around phosphorus in P(III) compounds generally falls in the range 295–300°.[16] The corresponding sums in **1** and **2** are not unusual in this respect (298.5 and 298.8°, respectively).

6

The He I UV PE spectra of **1** and **2** are shown in Figure 2, and in Table V the band assignments for these and related molecules[2,21,22] including **7**[23] are given. The values of IE_N bracket fairly closely the value for $Me_2N(POMe)_2$. All three of these values are larger than the average of the IE_N for $(Me_2N)_2POMe$ (8.48 eV) as might be expected from the presence in the latter of a second electron-donating Me_2N group and one less alkoxy linkage on phosphorus. Although the average of the first two values of IE_N for $P(NMe_2)_3$ is lower than the IE_N energies for **1**, **2**, or $Me_2NP(OMe)_2$, the third IE_N value for $P(NMe_2)_3$ is unexpectedly higher. Interaction of this level with the phosphorus lone-pair level has been cited as a possible cause for this high value.[2] Each decrement in IE_P from $P(OMe)_3$ to $Me_2NP(OMe)_2$ to $(Me_2N)_2POMe$ is ca. 0.3 eV. Assuming the decrease from the last compound to $P(NMe_2)_3$ is the same, then IE_P for $P(NMe_2)_3$ is ~8.3 eV. Taking the difference between this value and the assigned IE_P and correcting accordingly the 9.90-eV value for IE_N lead to an average IE_N for $P(NMe_2)_3$ of 8.6 eV. This is ~0.3 eV higher than anticipated. However, it should be realized (see Scheme IVa in ref 2a) that one of the nitrogens is tetrahedral, thus leading to an increased IE for this particular lone pair.



7

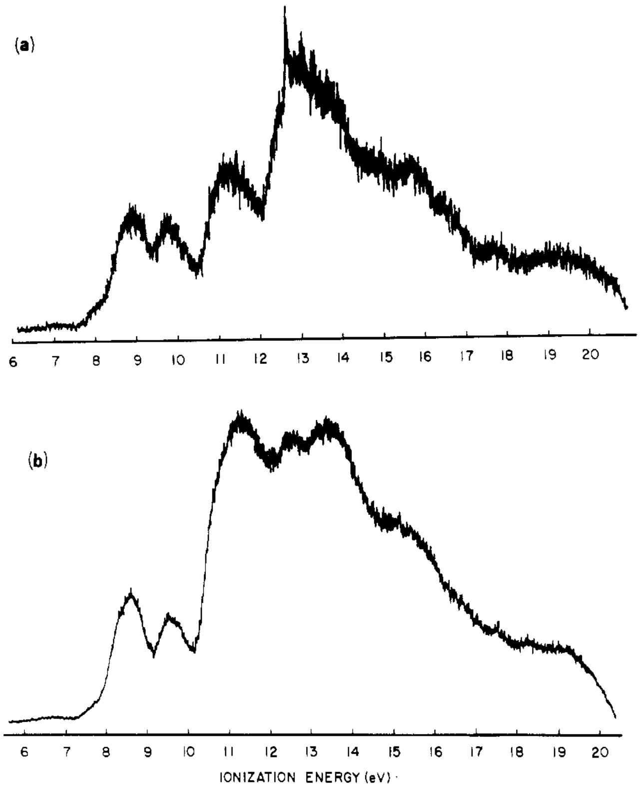


Figure 2. He I UV photoelectron spectra of (a) **1** and (b) **2**.

The PE spectral assignments for **1** and **2** parallel those reported recently for $Me_2NP(OMe)_2$[21a] and **7**[23] (see Table V). The lack of a clear comparison in the basicities between the cyclic compounds **1**, **2**, and **7** and the acyclic $Me_2NP(OMe)_2$ based on IE_P values may be obscured in part by the breadth of the bands in the low-energy region of the cyclic systems stemming from the overlap of the IE_N and IE_P bands. Except for **1**, the IE_P values for the cyclic systems in Table V fall below that of $Me_2NP(OMe)_2$ and this may be suggestive of greater phosphorus basicity in the R_2N-equatorial confor-

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(20) For a compilation of N–P bond lengths, see, e.g.: Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 133.

(21) (a) Worley, S. D.; Hargis, J.; Chang, L.; Mattson, G. A.; Jenning, W. B. *Chem. Phys. Lett.* **1971**, *93*, 6772. (b) Cowley, A. H.; Goodman, D. W.; Kuebler, N. A.; Sanchez, M.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 854.

(22) Cowley, A. H.; Lattman, M.; Montag, R. A.; Verkade, J. G. *Inorg. Chim. Acta* **1977**, *25*, L151.

(23) Arshinova, R. P.; Zverev, V. V.; Villem, Ya. Ya.; Villem, N. Y. *J. Gen. Chem. USSR (Engl. Transl.)* **1981**, *51*, 1503.

(24) White, D. W.; Bertrand, R. D.; McEwen, G. K.; Verkade, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 7125.

Table VI. ^{31}P NMR Chemical Shifts and $^{1}J_{^{31}P^{77}Se}$ Coupling Constants (Hz)

	$\delta(^{31}P)$	$^{1}J_{^{31}P^{77}Se}$		$\delta(^{31}P)$	$^{1}J_{^{31}P^{77}Se}$
$SeP(OMe)_3$[a]	78.0	954	**1a**[b]	79.2	914
8a[a]	68.6	985	**2a**[b]	76.9	909
9a[a]	66.8	996	**3a**[b]	75.1	895
10a[a]	68.8	949	**4a**[b]	77.6	924
$Me_2N(Se)P(OMe)_2$[b]	87.1	903	$SeP(NMe_2)_3$[a]	82.5	784

[a] See reference 4. [b] This work.

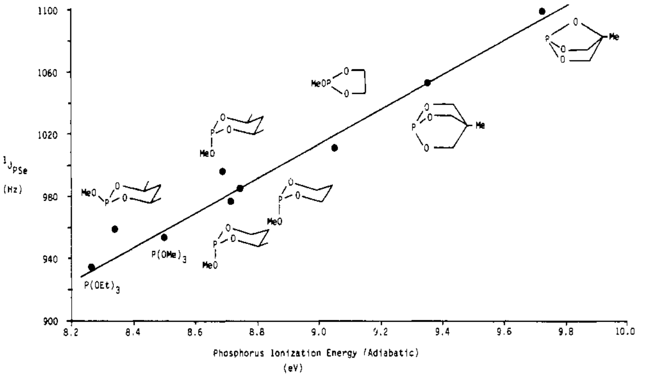
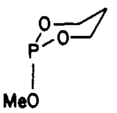
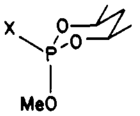


Figure 3. Plot of the adiabatic IE_P values of the phosphite esters shown vs. the $^{1}J_{PSe}$ values of their corresponding selenophosphates[27] (r^2 = 0.98).

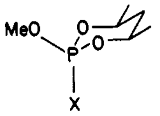
mation of such compounds relative to that of the acyclic analogue. Such a conclusion would accord with the greater basicity of **10** vs. that of $P(OMe)_3$ as shown by a comparison



8: X = lone pair
8a: X = Se

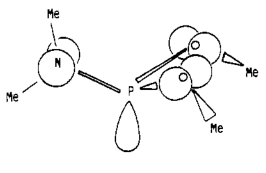


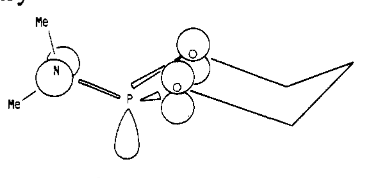
9: X = lone pair
9a: X = Se



10: X = lone pair
10a: X = Se

of their adiabatic IE_P (ΔIE_P = 0.16 eV) and gas-phase proton affinity values (ΔPA = 4.6 kcal/mol).[5b] In an attempt to determine the validity of the basicity comparison of **1** and **2** with respect to $Me_2NP(OMe)_2$, the $^{1}J_{PSe}$ values for their selenide derivatives were obtained. The NMR data for these and the related compounds **3a**, **4a**, and **8a**–**10a** are collected in Table VI. In agreement with earlier results, $^{1}J_{PSe}$ decreases upon substitution of the more electronegative MeO groups by Me_2N.[4] Moreover, comparison of the adiabatic IE_P data for a series of phosphite esters[5b] with the $^{1}J_{PSe}$ values for the corresponding selenophosphates[4] reveals the linear relationship shown in Figure 3. In this figure it is seen that **10** is somewhat more basic than $P(OMe)_3$. The larger $^{1}J_{PSe}$ vaues for **1a** and **2a** in Table VI at first glance suggest an opposite relationship regarding the relative basicities of the ring compounds **1** and **2** relative to $Me_2NP(OMe)_2$, namely, that **1** and **2** are less basic than the acyclic analogue. Such a conclusion would contradict rather than support the tentative conclusion reached from the UV PE spectral studies described here. It should be noted, however, that **1a** and **2a** may be in equilibria with chair conformations having opposite stereochemistries at phosphorus (i.e., equatorial Se and axial R_2N) which would possess higher $^{1}J_{PSe}$ values. Thus $^{1}J_{SPe}$ for the conformationally rigid **4a** is 924 Hz. For the equatorial R_2N conformation present in **1a** and **2a**, the $^{1}J_{PSe}$ values for the conformationally rigid **3a** (895 Hz) should be much more representative, and it is noteworthy that its coupling value is indeed less than that of $Me_2NP(OMe)_2$ (903 Hz) by 8 Hz. This difference exceeds that (5 Hz) between **10a** (949 Hz) and $SeP(OMe)_3$ (954 Hz). This larger difference in $^{1}J_{PSe}$ is made more significant by the fact that the absolute values of these couplings in the aminophosphite compounds are smaller than in their phosphite ester analogues. From the above considerations, it appears that the phosphorus in **1**, **2**, and **7** is more basic than in $Me_2NP(OMe)_2$ and this conclusion parallels the basicity relationship between **10** and $P(OMe)_3$ described earlier.[5b] The possible origin of this type of basicity difference has been discussed previously for phosphite esters in terms of interactions between the phosphorus lone pair and those on the heteroatoms.[25] It is interesting in this respect that the conformation of $Me_2NP(OMe)_2$ calculated by semiempirical MNDO methods is of the symmetry[21a]





The structural results reported here for **1** and **2**, and the similar conformation calculated by CNDO/2 methods for **7**,[26] are summarized in the structure shown. From the conformations of the lone-pair orbitals in the acyclic and cyclic structures it can be inferred that larger oxygen–phosphorus lone-pair–lone-pair interactions occur in the cyclic compounds (**1**, **2**, and **7**), thus augmenting the basicity of phosphorus in such systems relative to that in $Me_2NP(OMe)_2$.

It is germane to the present study to ask whether the parent compounds **1** (which is ~90% in the equatorial-Me_2N conformation as judged in this work by the ca. 9:1 equilibrium ratio of 3:4) and **8** (which is ~100% in the axial MeO conformation as judged by the exclusive presence of **9** upon equilibration of **9** and **10**) retain these conformations in the gas phase wherein the PE spectra are measured. That the PE spectrum of **8** is representative of the axial MeO conformation is supported by the observation that **8** and **9** have similar IE_P and proton affinity values in contrast to **10**.[5b] In view of the solid-state conformation of **1** and **2** described here and the previously reported conclusion that the stable diastereomer of **3** is as shown,[8] it is reasonable to assume that **1** and **2** preserve equatoriality of the dialkylamino group in the gas phase. Steric factors appear to dominate in the solid and solution phases, and there is no reason to suppose that electronic factors would become dominant in the gas phase.

Acknowledgment. We are grateful to the National Science Foundation for generous support of this research.

Registry No. **1**, 56465-64-6; **1a**, 91670-70-1; **2**, 56423-67-7; **2a**, 91670-71-2; **3**, 41158-14-9; **3a**, 91670-72-3; **4**, 41158-13-8; **4a**, 91740-04-4; $Me_2NP(OMe)_2$, 20217-54-3; $Me_2N(Se)P(OMe)_2$, 56595-15-4; $(MeO)_2PCl$, 3743-07-5; Me_2NH, 124-40-3.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors and computer drawings of the unit cells (14 pages). Ordering information is given on any current masthead page.

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(25) Verkade, J. G. *Phosphorus Sulfur* **1976**, *2*, 251.

(26) Arshinova, R. P. *J. Gen. Chem. USSR (Engl. Transl.)* **1978**, *238*, 47.

(27) The adiabatic IE_P data were taken from ref 5b except for $P(OEt)_3$[22] and $MeO\overline{POCHMeCH_2CH_2O}$.[23] In these references vertical IE_P values are reported and these were adjusted for Figure 3 by subtracting 0.66 eV, the correction factor being the average of the differences between the adiabatic values for $P(OMe)_3$[5b] and $P(OCH)_{23}CMe$[5b] and the vertical values reported for $P(OMe)_3$[22] and $P(OCH_2)_3CMe$ from experimental data originally reported by us,[21b] as reassigned on the basis of the MO calculations (Yarbrough, L. W.; Hall, M. B. *J. Chem. Soc., Chem. Commun.* **1978**, 161) and confirmed on the basis of PE spectral studies of additional compounds (Cowley, A. H.; Lattman, M.; Montag, R. A.; Verkade, J. G. *Inorg. Chem.*, following paper in this issue). The $^{1}J_{PSe}$ data on the selenophosphates were taken from ref 4 except for $SP(OEt)_3$ (Stec, W. J.; Okruszek, A.; Uznanski, B.; Michalski, J. *Phosphorus Relat. Group V Elem.* **1972**, *2*, 97) and $MeO(Se)\overline{POCHMeCH_2CH_2O}$ (Stec, W. J. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1974**, *29B*, 109).