

Structural Studies on the Phosphorus—Nitrogen Bond. II. The Crystal Structure of Tris(morpholino)phosphine Selenide, Tris(piperidino)phosphine Selenide and Tris(dimethylamino)-phosphine Selenide

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The structures of the title compounds, $[\text{O}(\text{CH}_2\text{CH}_2)_2\text{N}]_3\text{PSe}$, I, $[\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{N}]_3\text{PSe}$, II, and $[(\text{CH}_3)_2\text{N}]_3\text{PSe}$, III, have been determined from X-ray data. Full-matrix least-squares refinement led to final conventional *R*-values of 0.032 (2954) for I, 0.024 (4255) for II and 0.047 (2735) for III. (The number of observed reflections in parenthesis.)

The compounds crystallize in the monoclinic system with the following unit cell dimensions: I (at 18 °C): $a=8.635(2)$ Å, $b=14.942(3)$ Å, $c=12.304(3)$ Å and $\beta=100.33(2)^\circ$. II (at -150 °C): $a=13.159(2)$ Å, $b=15.305(2)$ Å, $c=9.371(1)$ Å, $\beta=112.40(1)^\circ$. III (at -150 °C): $a=8.376(2)$ Å, $b=11.496(2)$ Å, $c=11.406(2)$ Å, $\beta=93.65(2)^\circ$. The space groups are $P2_1/c$ for I, $P2_1/n$ for II and $P2_1/n$ for III, and the number of molecules per unit cell is four.

There are in all three compounds two short P–N bonds, 1.65–1.66 Å, and one longer P–N bond, 1.68 Å. The nitrogen atom linked to the phosphorus atom through a long bond is essentially sp^3 hybridized in each compound; the two remaining nitrogen atoms are intermediate between sp^2 and sp^3 hybridized in I, whereas these two nitrogen atoms are essentially sp^2 hybridized in II and III.

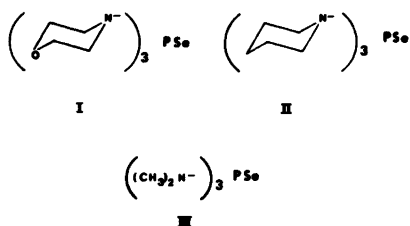
The lone pair direction of the sp^3 hybridized nitrogen atom is in all three compounds strictly *anti* to the P–Se bond, whereas the lone pairs of the remaining nitrogen atoms are roughly orthogonal to the P–Se bond. None of the compounds is symmetrical with regard to the NPN bond angles, the largest angle being the one not including the sp^3 hybridized nitrogen atom. The sum of the NPN angles are 317.7, 317.1 and 318.1° in I, II and III,

respectively, as compared to 306.6 and 305.0° for the unselenated analogues of I and II.

The P–Se bond lengths are 2.106(1), 2.1110(4) and 2.120(1) Å in I, II and III, respectively.

In Part I of this series the crystal and molecular structures of tris(morpholino)phosphine and tris(piperidino)phosphine were described.¹ It was shown that these crystalline aminophosphines do not possess C_3 local symmetry but are highly asymmetric compounds containing at least two different nitrogen atoms (essentially sp^3 and sp^2 hybridized, respectively), two different P–N bond lengths and two different NPN bond angles.

In an attempt to further examine the various factors governing not only the length of the P–N bonds, but also the asymmetry of phosphorus compounds in which the phosphorus atom is linked to three nitrogen atoms, we have turned to pentacovalent compounds. Only one structure determination of this class of compounds seems to have been carried out so far, that of tris(aziridino)phosphine sulfide.² This compound, however, is atypical for the usual tris(dialkylamino)phosphine chalcogenides since the nitrogen atoms are locked in their conformation in the three-membered aziridino rings. In the present study we want to report the crystal and molecular structure determination of tris(morpholino)phosphine selenide, I, tris(piperidino)phosphine selenide, II, and tris(dimethylamino)phosphine selenide, III.



Scheme 1.

The selenides were chosen since III, as are I and II, is a nicely crystalline compound at room temperature in contrast to the corresponding sulfide. It appeared especially interesting to compare the structure of III to that of I and II since a similarity in structure might strengthen the previous assumption that the structure of tris(morpholino)phosphine and tris(piperidino)phosphine is characteristic for tris(dialkylamino)phosphines, $(R_2N)_3P$, generally.¹ Furthermore, the selenides are simple to prepare and are very stable for long periods of time; no pink colourization of the crystals due to elemental selenium could be observed.

EXPERIMENTAL

Materials. Tris(morpholino)phosphine selenide, I, was prepared as previously described.³ Suitable crystals were grown from acetonitrile at room temperature. The specimen used for the X-ray experiments was cut to dimensions $0.32 \times 0.40 \times 0.40$ mm.

Tris(piperidino)phosphine selenide, II, apparently a new compound, was made from the parent aminophosphine and black selenium powder in dry cyclohexane at room temperature. The mixture was stirred until nearly all the selenium had dissolved (about 30 min). After filtration, the product was precipitated with pentane at 0°C in close to quantitative yield. Crystals suitable for the X-ray experiments were obtained from an ethanolic solution at 0°C . (Found: C 49.83; H 8.28; N 11.07. Calc. for $C_{15}H_{30}N_3PSe$: C 49.72; H 8.35; N 11.60.) The specimen used for the structure determination was ground to a sphere with diameter 0.40 mm.

Tris(dimethylamino)phosphine selenide, III, was prepared as described in Ref. 4. Suitable crystals were obtained from light petroleum ($40-60^\circ\text{C}$); a crystal with dimensions $0.1 \times 0.3 \times 0.4$ mm was used for the experimental work.

X-Ray data. Data for the measurement of cell dimensions and intensity data were collected on a Picker punched card controlled four-circle diffrac-

tometer at $18 \pm 1^\circ\text{C}$ for compound I and on a SYNTEX PI diffractometer with -150°C at the crystal site for compounds II and III, using graphite crystal monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Intensity data were collected with the $\theta-2\theta$ scan technique, scan speeds (2θ) were 2° min^{-1} for I, $3-6^\circ \text{ min}^{-1}$ for II and $2-4^\circ \text{ min}^{-1}$ for III, the scan speed for II and III depending on the intensity; scan widths were 1.4° (I), 1.6° (II) and 2.4° (III). For compound I all intensities in a quadrant of reciprocal space within $\sin \theta/\lambda = 0.7 \text{ \AA}^{-1}$ were measured; for II and III all unique reflections were recorded up to $\sin \theta/\lambda = 0.54 \text{ \AA}^{-1}$ and for higher angles up to a $\sin \theta/\lambda$ value of 0.7 \AA^{-1} for II and 0.76 \AA^{-1} for III the intensities were measured only if larger than a preset value according to a quick scan. Background counts were taken at each of the scan limits for 30 s for compound I and for 0.35 times the scan time for II and III. Three standard reflections were measured after every 100 reflections; for data set I a decrease of 17% in the intensities of the standard reflections was observed, for II and III variations of 1 and 2%, respectively, were observed. The intensities of the data sets were adjusted according to the drift in the standard reflections. The numbers of reflections recorded for the three compounds were 3602, 4409 and 3169 for I, II and III, respectively. Of these 2954 (I), 4255 (II) and 2735 (III) with $I > 2.5 \sigma(I)$ were retained for the structure determinations. The estimate of the standard deviation of the intensity was based on counting statistics with an additional term of 2% of the net intensity. The data were corrected for Lorentz and polarization effects, and also for absorption.

A description of the computer programs applied for the structure analyses is given in Ref. 5. The quantity minimized in the full-matrix least-squares program was $\sum w \Delta F^2$, where w is the inverse of the variance of the observed structure factor. In order to reduce the weights of low-order reflections w was multiplied with a factor varying from 0 to 1 for reflections with $\sin \theta/\lambda$ from 0 to 0.45 \AA^{-1} .

Atomic form factors were those of Doyle and Turner⁶ for Se, P, O, N and C, and of Stewart, Davidson and Simpson⁷ for H.

CRYSTAL DATA

I. Tris(morpholino)phosphine selenide, $C_{12}H_{24}N_3O_3PSe$, m.p. 157°C . Monoclinic, $a = 8.635(2) \text{ \AA}$; $b = 14.942(3) \text{ \AA}$; $c = 12.304(3) \text{ \AA}$; $\beta = 100.33(2)^\circ$; $V = 1561.8 \text{ \AA}^3$; ($t = 18 \pm 1^\circ\text{C}$). $M = 368.27$; $Z = 4$; $F(000) = 760$; $\mu(\text{MoK}\alpha) = 27.0 \text{ cm}^{-1}$; $D_x = 1.566 \text{ g cm}^{-3}$. Space group $P2_1/c$ (No. 14).

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations for tris(morpholino)phosphine selenide (I), tris(piperidino)phosphine selenide (II) and tris(dimethylamino)phosphine selenide (III). The anisotropic temperature factor is given by $\exp -2\pi^2(U_{11}a^*{}^2h^2 + \dots + 2U_{12}a^*b^*hk + \dots)$.

I									
ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
SE	.59583(3)	.78380(2)	.66182(2)	.0432(2)	.0395(2)	.0459(2)	-.0130(1)	-.0031(1)	.0036(1)
P	.79231(7)	.86457(3)	.72113(4)	.0330(3)	.0249(3)	.0236(2)	-.0017(2)	.0017(2)	.0008(2)
O1	1.2370(2)	.7015(1)	.7917(2)	.0418(10)	.0431(10)	.0599(12)	.0093(8)	.0083(8)	-.0020(8)
O2	.7084(2)	.9620(1)	1.0512(1)	.0528(11)	.0501(10)	.0326(9)	.0116(8)	.0164(8)	.0070(7)
O3	.8294(2)	1.0783(1)	.4962(2)	.0548(11)	.0425(9)	.0422(10)	-.0035(8)	.0067(8)	.0141(8)
N1	.9586(2)	.8064(1)	.7420(2)	.0381(10)	.0296(9)	.0733(10)	.0014(8)	.0008(8)	-.0068(7)
N2	.7929(2)	.9111(1)	.8456(1)	.0379(10)	.0286(9)	.0242(8)	.0040(7)	.0045(7)	.0029(7)
N3	.7963(2)	.9552(1)	.6426(1)	.0431(11)	.0285(9)	.0231(9)	-.0046(8)	.0034(8)	.0002(7)
C11	.9781(3)	.7236(2)	.6813(2)	.0508(14)	.0431(13)	.0362(12)	.0056(11)	.0021(11)	-.0118(10)
C12	1.0879(3)	.6624(2)	.7546(2)	.0477(15)	.0333(12)	.0556(16)	.0056(11)	.0080(12)	-.0053(11)
C13	1.2208(3)	.7817(2)	.8509(2)	.0402(13)	.0458(14)	.0510(15)	.0036(11)	-.0014(11)	-.0052(12)
C14	1.1133(3)	.8488(2)	.7814(2)	.0376(12)	.0384(12)	.0469(13)	-.0029(11)	.0039(11)	-.0045(10)
C21	.6636(3)	.9746(2)	.8513(2)	.0409(13)	.0381(12)	.0338(12)	.0097(10)	.0082(10)	.0071(9)
C22	.6932(3)	1.0228(2)	.9605(2)	.0460(14)	.0387(12)	.0390(13)	.0053(10)	.0136(11)	.0034(10)
C23	.8321(3)	.8998(2)	1.0463(2)	.0433(14)	.0517(14)	.0299(11)	.0095(11)	.0076(10)	.0062(10)
C24	.8053(3)	.8480(2)	.9393(2)	.0448(13)	.0364(12)	.0301(11)	.0067(10)	.0075(10)	.0081(9)
C31	.9154(3)	1.0255(2)	.6727(2)	.0494(14)	.0338(11)	.0322(11)	-.0103(10)	.0040(10)	.0007(9)
C32	.8613(4)	1.1116(2)	.6116(2)	.0590(16)	.0322(12)	.0511(15)	-.0029(11)	.0152(13)	.0011(11)
C33	.7117(3)	1.0322(2)	.4677(2)	.0468(15)	.0594(17)	.0439(14)	-.0065(13)	-.0008(12)	.0188(12)
C34	.7603(3)	.9438(2)	.5215(2)	.0512(14)	.0419(12)	.0229(11)	-.0069(11)	.0034(10)	.0021(9)

II									
ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H111	1.016(4)	.739(2)	.611(3)	3.4(2)	H112	.882(4)	.692(2)	.657(3)	3.4
H121	1.105(4)	.608(2)	.724(3)	3.7(2)	H122	1.036(4)	.650(2)	.819(3)	3.7
H131	1.321(4)	.802(2)	.873(3)	3.7	H132	1.173(4)	.772(2)	.924(3)	3.7
H141	1.166(4)	.860(2)	.719(3)	3.4	H142	1.097(4)	.901(2)	.819(3)	3.4
H211	.563(4)	.945(2)	.844(3)	3.4	H212	.658(4)	1.020(2)	.788(3)	3.4
H221	.609(4)	1.063(2)	.965(3)	3.7	H222	.789(4)	1.055(2)	.965(3)	3.7
H231	.833(4)	.854(2)	1.107(3)	3.7	H232	.931(4)	.929(2)	1.053(3)	3.7
H241	.716(4)	.817(2)	.934(3)	3.4	H242	.890(4)	.807(2)	.938(3)	3.4
H311	1.011(4)	1.005(2)	.651(3)	3.4	H312	.925(4)	1.040(2)	.753(3)	3.4
H321	.946(4)	1.157(2)	.630(3)	3.7	H322	.772(4)	1.130(2)	.632(3)	3.7
H331	.694(4)	1.025(2)	.382(3)	3.7	H332	.628(4)	1.051(2)	.490(3)	3.7
H341	.847(4)	.923(2)	.497(3)	3.4	H342	.679(4)	.903(2)	.501(3)	3.4

III									
ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
SE	.12959(1)	.23361(1)	.14281(2)	.0174(1)	.0212(1)	.0196(1)	.0247(1)	.0719(1)	.0068(1)
N1	.21584(3)	.14436(2)	.31257(4)	.0115(1)	.0136(1)	.0138(1)	.0316(1)	.0931(1)	.0012(1)
N2	.26794(10)	.19063(8)	.48454(13)	.0210(5)	.0154(5)	.0149(5)	.0049(4)	.0035(4)	-.0000(4)
N3	.32343(9)	.18896(8)	.28364(13)	.0122(5)	.0157(5)	.0157(5)	.0078(4)	.0039(4)	.0022(4)
N4	.14581(9)	.85514(8)	.31756(14)	.0150(5)	.0164(5)	.0235(6)	.0001(4)	.0074(4)	.0011(4)
C11	.33599(12)	.13681(11)	.61896(16)	.0210(6)	.0191(7)	.0155(6)	.0048(5)	.0022(5)	.0002(5)
C12	.29362(14)	.14859(11)	.74824(18)	.0292(8)	.0269(9)	.0212(7)	.0036(6)	.0107(6)	.0056(6)
C13	.29091(18)	.24426(12)	.79084(20)	.0498(11)	.0334(9)	.0238(7)	.0128(8)	.0184(7)	.0009(6)
C14	.22476(18)	.29744(13)	.64718(21)	.0489(11)	.0278(8)	.0278(8)	.0164(8)	.0189(8)	.0014(7)
C15	.26789(14)	.28388(9)	.51916(18)	.0294(7)	.0154(6)	.0225(7)	.0008(5)	.0102(6)	-.0010(5)
C21	.41767(11)	.15977(9)	.31062(17)	.0146(6)	.0169(6)	.0218(6)	.0025(5)	.0066(5)	-.0035(5)
C22	.81943(11)	.18645(10)	.32825(17)	.0130(6)	.0253(7)	.0214(6)	.0002(5)	.0046(5)	-.0010(5)
C23	.49917(12)	.05191(10)	.18405(17)	.0191(6)	.0213(7)	.0224(7)	.0028(5)	.0097(5)	.0008(5)
C24	.39704(13)	-.00441(10)	.14925(19)	.0268(7)	.0197(7)	.0262(7)	.0025(5)	.0141(6)	-.0056(6)
C25	.29823(12)	.35894(10)	.13928(17)	.0178(6)	.0236(7)	.0176(6)	.0042(5)	.0064(5)	-.0042(5)
C31	.03378(12)	.06437(10)	.31322(20)	.0196(7)	.0214(7)	.0369(8)	.0006(5)	.0155(6)	.0000(7)
C32	-.04021(13)	-.00693(12)	.21294(21)	.0172(7)	.0364(9)	.0313(8)	.0058(6)	.0092(6)	-.0009(7)
C33	.08505(14)	-.39771(11)	.26726(21)	.0269(8)	.0271(8)	.0323(8)	.0115(6)	.0147(6)	-.0102(6)
C34	.12492(14)	-.10322(11)	.26851(22)	.0278(8)	.0187(7)	.0428(9)	.0038(6)	.0175(7)	-.0069(7)
C35	.19415(12)	-.02986(9)	.37969(18)	.0203(7)	.0169(6)	.0265(7)	-.0021(5)	.0072(6)	.0035(5)

IV									
ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H111	.410(2)	.160(1)	.651(2)	2.0(1)	H112	.335(2)	.078(1)	.598(2)	2.0
H121	.336(2)	.115(2)	.834(3)	2.6(1)	H122	.217(2)	.125(2)	.714(3)	2.6
H131	.366(2)	.267(2)	.836(3)	2.6(2)	H132	.261(2)	.248(2)	.866(3)	2.6
H141	.227(2)	.360(2)	.669(3)	2.6	H142	.149(2)	.279(2)	.608(3)	2.6
H151	.345(2)	.305(1)	.552(2)	2.0	H152	.222(2)	.312(1)	.425(2)	2.0
H211	.430(2)	.193(1)	.401(2)	2.0	H212	.493(2)	.198(1)	.223(2)	2.0
H221	.536(2)	.070(2)	.417(3)	2.6	H222	.583(2)	.145(2)	.349(3)	2.6
H231	.563(2)	.316(2)	.194(3)	2.6	H232	.497(2)	.891(2)	.098(3)	2.6
H241	.410(2)	-.048(2)	.228(3)	2.6	H242	.379(2)	-.838(2)	.851(3)	2.6
H251	.237(2)	.014(1)	.123(2)	2.0	H252	.280(2)	.891(1)	.844(2)	2.0
H311	.000(2)	.120(1)	.278(2)	2.0	H312	.635(2)	.068(1)	.420(2)	2.0
H321	-.346(2)	.064(2)	.114(3)	2.6	H322	-.114(2)	.080(2)	.215(3)	2.6
H331	-.938(2)	-.148(2)	.186(3)	2.6	H332	.084(2)	-.087(2)	.369(3)	2.6
H341	.180(2)	-.899(2)	.173(3)	2.6	H342	.158(2)	-.159(2)	.324(3)	2.6
H351	.270(2)	-.832(1)	.382(2)	2.0	H352	.197(2)	-.038(1)	.488(2)	2.0

Table 1. Continued.

III									
ATOM	x	y	z	U11	U22	U33	U12	U13	U23
SE	.46817(4)	.13535(3)	.21435(3)	.0281(2)	.0311(2)	.0211(2)	.0025(2)	.0007(1)	-.0104(1)
P	.47732(9)	.23996(7)	.36703(6)	.0139(3)	.0173(4)	.0139(3)	.0011(3)	.0007(2)	-.0007(3)
N1	.5765(3)	.3658(2)	.3546(2)	.0180(11)	.0189(12)	.0211(11)	-.0003(11)	.0025(9)	.0002(11)
N2	.5638(3)	.1688(2)	.4794(2)	.0205(12)	.0231(13)	.0201(12)	.0010(10)	-.0017(10)	.0024(10)
N3	.3001(3)	.2864(3)	.4019(2)	.0150(11)	.0238(13)	.0220(12)	.0022(10)	.0024(9)	-.0002(11)
C11	.7515(4)	.3536(3)	.3595(3)	.0185(14)	.0275(18)	.0347(17)	-.0039(14)	.0065(12)	-.0032(16)
C12	.5170(5)	.4421(3)	.2581(3)	.0367(20)	.0282(19)	.0261(17)	-.0005(16)	.0044(15)	.0085(14)
C21	.5521(5)	.2119(4)	.5995(3)	.0378(20)	.0376(21)	.0182(15)	-.0012(18)	-.0055(13)	.0025(15)
C22	.6868(5)	.0802(4)	.4700(4)	.0283(18)	.0309(20)	.0390(20)	.0088(16)	-.0039(15)	.0081(17)
C31	.1651(4)	.2070(3)	.3972(3)	.0156(14)	.0317(18)	.0296(17)	-.0013(13)	.0014(12)	.0017(15)
C32	.2714(5)	.3937(3)	.4461(3)	.0287(17)	.0268(18)	.0318(17)	.0052(14)	.0102(14)	-.0040(14)

ATOM	x	y	z	B	ATOM	x	y	z	B
H111	.793(6)	.310(5)	.433(5)	3.1(2)	H112	.797(6)	.429(5)	.357(4)	3.1
H113	.787(6)	.306(5)	.297(5)	3.1	H121	.403(7)	.452(5)	.262(4)	3.1
H122	.556(6)	.424(5)	.191(5)	3.1	H123	.571(6)	.518(5)	.272(4)	3.1
H211	.465(6)	.268(5)	.604(4)	3.1	H212	.636(7)	.257(5)	.622(5)	3.1
H213	.541(6)	.145(5)	.650(5)	3.1	H221	.686(6)	.052(5)	.391(5)	3.1
H222	.665(6)	.014(5)	.521(5)	3.1	H223	.798(7)	.112(5)	.502(5)	3.1
H311	.181(6)	.138(5)	.345(5)	3.1	H312	.065(6)	.249(5)	.362(5)	3.1
H313	.140(6)	.186(5)	.473(5)	3.1	H321	.365(6)	.438(5)	.475(4)	3.1
H322	.224(6)	.379(4)	.539(5)	3.1	H323	.184(6)	.437(5)	.422(5)	3.1

II. Tris(piperidino)phosphine selenide, $C_{15}H_{30}N_3PSe$, m.p. 121–122 °C. Monoclinic, $a = 13.159(2)$ Å; $b = 15.305(2)$ Å; $c = 9.371(1)$ Å; $\beta = 112.40(1)^\circ$; $V = 1745.0$ Å³; ($t = -150$ °C). $M = 362.36$; $Z = 4$; $F(000) = 760$; $\mu(MoK\alpha) = 24.0$ cm⁻¹; $D_x = 1.379$ g cm⁻³. Space group $P2_1/n$ (No. 14).

III. Tris(dimethylamino)phosphine selenide, $C_6H_{18}N_3PSe$, m.p. 51–52 °C. Monoclinic, $a = 8.376(2)$ Å; $b = 11.496(2)$ Å; $c = 11.406(2)$ Å; $\beta = 93.65(2)^\circ$; $V = 1096.1$ Å³; ($t = -150$ °C). $M = 242.16$; $Z = 4$; $F(000) = 496$; $\mu(MoK\alpha) = 37.8$ cm⁻¹; $D_x = 1.467$ g cm⁻³. Space group $P2_1/n$ (No. 14).

STRUCTURE DETERMINATIONS

The structures were determined by Patterson methods followed by successive Fourier syntheses.

Refinements were performed in the way described in Ref. 1; they converged to conventional R -factors of 0.032 for I, 0.024 for II and 0.047 for III. The R_w -values were 0.038 (I), 0.029 (II) and 0.047 (III), and the S -values $[\sum w\Delta F^2/(m-n)]^{1/2}$, were 1.90, 1.56 and 1.99, respectively. The overdetermination ratios were 11.6 (I), 15.6 (II) and 17.6 (III).

Analyses of the rigid body vibrations of the molecules were carried out; for the discussion of the structures bond lengths corrected for libration are used.

Final atomic parameters are listed in Table 1. Tables of observed and calculated structure factors with standard deviations are available from the authors.

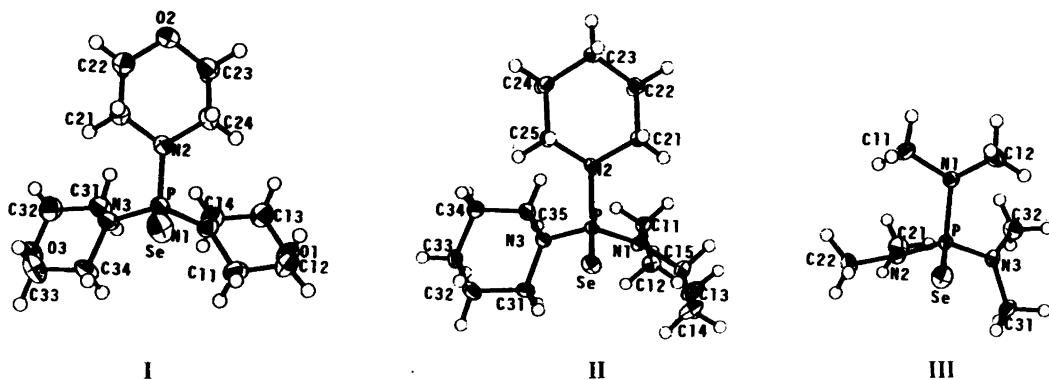


Fig. 1. ORTEP drawings of tris(morpholino)phosphine selenide (I), tris(piperidino)phosphine selenide (II) and tris(dimethylamino)phosphine selenide (III).

Table 2. Structural data.

Bond lengths (Å)

I				II				III			
			corr.				corr.				corr.
P	Se	2.103(1)	2.106	P	Se	2.1090(4)	2.1110	P	Se	2.114(1)	2.120
P	N1	1.659(2)	1.661	P	N1	1.651(1)	1.653	P	N1	1.678(3)	1.682
P	N2	1.681(2)	1.684	P	N2	1.677(1)	1.678	P	N2	1.649(3)	1.652
P	N3	1.668(2)	1.670	P	N3	1.658(1)	1.660	P	N3	1.650(3)	1.654
N1	C11	1.469(3)	1.471	N1	C11	1.469(2)	1.470	N1	C11	1.471(4)	1.474
C11	C12	1.498(4)	1.499	C11	C12	1.519(2)	1.520	N1	C12	1.470(5)	1.474
C12	O1	1.413(3)	1.415	C12	C13	1.523(3)	1.525	N2	C21	1.466(5)	1.469
O1	C13	1.422(3)	1.424	C13	C14	1.530(3)	1.531	N2	C22	1.458(5)	1.461
C13	C14	1.521(4)	1.522	C14	C15	1.524(2)	1.525	N3	C31	1.452(5)	1.454
C14	N1	1.480(3)	1.482	C15	N1	1.464(2)	1.465	N3	C32	1.462(5)	1.464
N2	C21	1.476(3)	1.478	N2	C21	1.474(2)	1.475	C-H (mean) 0.97(4)			
C21	C22	1.505(4)	1.507	C21	C22	1.524(2)	1.525				
C22	O2	1.426(3)	1.428	C22	C23	1.522(2)	1.524				
O2	C23	1.426(3)	1.427	C23	C24	1.524(2)	1.525				
C23	C24	1.509(4)	1.510	C24	C25	1.525(2)	1.526				
C24	N2	1.479(3)	1.480	C25	N2	1.478(2)	1.479				
N3	C31	1.470(3)	1.472	N3	C31	1.471(2)	1.472				
C31	C32	1.520(4)	1.521	C31	C32	1.519(2)	1.521				
C32	O3	1.411(3)	1.413	C32	C33	1.524(3)	1.525				
O3	C33	1.415(4)	1.416	C34	C34	1.526(2)	1.527				
C33	C34	1.503(4)	1.505	C35	C35	1.520(2)	1.521				
C34	N3	1.477(3)	1.479	C36	N3	1.468(2)	1.469				
C-H (mean) 0.96(5)				C-H (mean) 0.97(2)							

Bond angles (°)

I				II				III			
Se	P	N1	112.0(1)	Se	P	N1	111.40(4)	Se	P	N1	114.4(1)
Se	P	N2	115.1(1)	Se	P	N2	115.49(4)	Se	P	N2	110.4(1)
Se	P	N3	111.4(1)	Se	P	N3	112.20(5)	Se	P	N3	113.4(1)
N1	P	N2	102.4(1)	N1	P	N2	105.40(6)	N1	P	N2	107.3(1)
N2	P	N3	101.2(1)	N2	P	N3	101.01(6)	N2	P	N3	109.3(1)
N3	P	N1	114.1(1)	N3	P	N1	110.75(7)	N3	P	N1	101.5(1)
P	N1	C11	122.5(2)	P	N1	C11	119.7(1)	P	N1	C11	114.4(2)
P	N1	C14	122.1(2)	P	N1	C15	126.8(1)	P	N1	C12	115.6(2)
P	N2	C21	115.5(1)	P	N2	C21	116.0(1)	P	N2	C21	120.4(2)
P	N2	C24	115.8(1)	P	N2	C25	116.4(1)	P	N2	C22	124.6(2)
P	N3	C31	121.4(1)	P	N3	C31	119.1(1)	P	N3	C31	119.9(2)
P	N3	C34	117.9(1)	P	N3	C35	125.4(1)	P	N3	C32	125.0(2)
N1	C11	C12	109.0(2)	N1	C11	C12	110.1(1)	C11	N1	C12	112.0(3)
C11	C12	O1	112.5(2)	C11	C12	C13	110.9(1)	C21	N2	C22	113.3(3)
C12	O1	C13	110.3(2)	C12	C13	C14	110.1(1)	C31	N3	C32	113.4(3)
O1	C13	C14	112.0(2)	C13	C14	C15	111.3(1)				
C13	C14	N1	109.0(2)	C14	C15	N1	109.8(1)				
C14	N1	C11	110.3(2)	C15	N1	C11	112.0(1)				
N2	C21	C22	109.9(2)	N2	C21	C22	109.9(1)				
C21	C22	O2	111.8(2)	C21	C22	C23	110.3(1)				
C22	O2	C23	110.2(2)	C22	C23	C24	110.1(1)				
O2	C23	C24	111.9(2)	C23	C24	C25	111.2(1)				
C23	C24	N2	109.4(2)	C24	C25	N2	110.1(1)				
C24	N2	C21	108.8(2)	C25	N2	C21	110.7(1)				
N3	C31	C32	109.9(2)	N3	C31	C32	110.4(1)				
C31	C32	O3	111.5(2)	C31	C32	C33	111.5(1)				
C32	O3	C33	110.4(2)	C32	C33	C34	110.1(1)				
O3	C33	C34	111.9(2)	C33	C34	C35	111.5(1)				
C33	C34	N3	109.5(2)	C34	C35	N3	110.1(1)				
C34	N3	C31	110.4(2)	C35	N3	C31	111.9(1)				

Table 2. Continued.

Torsional angles ($^{\circ}$)

I				II				III						
Se	P	N1	C11	26.2(2)	Se	P	N1	C11	179.3(1)	Se	P	N1	C11	-75.4(2)
Se	P	N1	C14	178.7(2)	Se	P	N1	C15	-10.3(1)	Se	P	N1	C12	56.9(3)
Se	P	N2	C21	-63.3(2)	Se	P	N2	C21	73.2(1)	Se	P	N2	C21	-166.1(3)
Se	P	N2	C24	65.5(2)	Se	P	N2	C25	-59.7(1)	Se	P	N2	C22	30.1(3)
Se	P	N3	C31	174.9(2)	Se	P	N3	C31	-45.5(1)	Se	P	N3	C31	43.9(3)
Se	P	N3	C34	-43.4(2)	Se	P	N3	C35	157.6(1)	Se	P	N3	C32	-152.4(3)
N1	P	N2	C21	174.9(2)	N1	P	N2	C21	-50.2(1)	N1	P	N2	C21	68.6(3)
N1	P	N2	C24	-56.3(2)	N1	P	N2	C25	176.9(1)	N1	P	N2	C22	-95.2(3)
N1	P	N3	C31	-57.1(2)	N1	P	N3	C31	79.7(1)	N1	P	N3	C31	167.1(3)
N1	P	N3	C34	84.6(2)	N1	P	N3	C35	-77.3(1)	N1	P	N3	C32	-29.3(3)
N2	P	N1	C11	150.0(2)	N2	P	N1	C11	-54.7(1)	N2	P	N1	C11	47.5(3)
N2	P	N1	C14	-57.5(2)	N2	P	N1	C15	115.7(1)	N2	P	N1	C12	179.8(3)
N2	P	N3	C31	52.1(2)	N2	P	N3	C31	-169.0(1)	N2	P	N3	C31	-79.8(3)
N2	P	N3	C34	-166.2(2)	N2	P	N3	C35	34.0(1)	N2	P	N3	C32	83.9(3)
N3	P	N1	C11	-101.5(2)	N3	P	N1	C11	53.7(1)	N3	P	N1	C11	162.2(3)
N3	P	N1	C14	51.0(2)	N3	P	N1	C15	-135.9(1)	N3	P	N1	C12	-65.6(3)
N3	P	N2	C21	56.9(2)	N3	P	N2	C21	-165.6(1)	N3	P	N2	C21	-40.7(3)
N3	P	N2	C24	-174.3(2)	N3	P	N2	C25	61.6(1)	N3	P	N2	C22	155.5(3)

Various derived and averaged data

Nx	I			II			III		
	N1	N2	N3	N1	N2	N3	N1	N2	N3
$\overline{N-C}$ (Å)	1.477	1.479	1.476	1.468	1.477	1.471	1.474	1.465	1.459
$\overline{C-C}$ (Å)	1.511	1.509	1.513	1.525	1.525	1.524			
$\overline{C-O}$ (Å)	1.420	1.428	1.415						
Deviation of Nx from plane PCC (Å)	0.20	0.40	0.29	0.07	0.37	0.17	0.38	0.12	0.12
Sum of Nx bond angles ($^{\circ}$)	354.9	340.1	349.7	359.4	343.1	356.4	342.0	358.2	358.3
Torsional angle Se-P-N-Lone pair(N) ($^{\circ}$)	-77.6	-178.9	65.8	84.5	-173.3	56.1	170.8	-68.0	-54.3
Sum of NPN angles ($^{\circ}$)		317.7			317.2			318.1	

Short intramolecular distances (Å)

I			II			III		
Se	H112(e)	2.84	Se	H152(e)	2.74	Se	H221	2.80
Se	H432(e)	2.86	Se	H311(e)	2.88	Se	H311	2.91
P	H112(e)	2.85	P	H112(e)	2.67	P	H111	2.82
P	H142(e)	2.75	P	H152(e)	2.77	P	H113	2.86
P	H212(e)	2.78	P	H211(e)	2.72	P	H121	2.77
P	H242(e)	2.78	P	H251(e)	2.76	P	H211	2.73
P	H312(e)	2.87	P	H311(e)	2.66	P	H221	2.79
P	H342(e)	2.78	P	H351(e)	2.80	P	H311	2.75
			N2	H351(e)	2.44	P	H321	2.78
						N1	H321	2.45

DISCUSSION

ORTEP drawings of the molecules are shown in Fig. 1, where the numbering of the atoms is also indicated. In Table 2 bond lengths, torsional angles and other structural data are listed. Estimated

standard deviations are calculated from the correlation matrices.

Crystal structure determinations of tris(morpholino)phosphine and tris(piperidino)phosphine have revealed that these compounds favour a

conformation with two nitrogen lone pairs nearly orthogonal to the phosphorus lone pair.¹ The lone pair of the third nitrogen atom is antiparallel to the phosphorus lone pair. In such a conformation the number of repulsive interactions between phosphorus and nitrogen lone pairs is at a minimum and the three nitrogen lone pairs are partly orthogonal to each other.

The results of the present study indicate that the structures of the corresponding pentavalent phosphorus compounds, the selenated aminophosphines ($R_2N)_3PSe$, are closely related to the structure of the parent aminophosphines. Similar to the trivalent phosphorus species,¹ these compounds do not possess C_3 local symmetry, but are highly asymmetric with regard to the NPN angles, the P–N bond lengths, the hybridization of the nitrogen atoms, the torsional angles and the SePN angles. This asymmetry does not appear to be due to neighbouring molecules in the crystalline state since there seems to be no especially close intermolecular contacts.

Apparently, in the pentavalent species the phosphorus–selenide bond, and presumably other phosphorus–chalcogenide bonds, exerts the same conformational influence as does the phosphorus lone pair in the corresponding trivalent phosphorus species when the phosphorus atom is linked to three nitrogen atoms. The only significant difference in the structures of I and II from the structures of the unselenated species appears to be the NPN bond angles, the sums of which are by 11–12° larger in the aminophosphine selenides (see below). The structure of tris(dimethylamino)phosphine selenide, III, is quite analogous to that of I and II; the close similarity in the structure of the compounds substantiates the previous conclusion that tris(dialkylamino)phosphines, $(R_2N)_3P$ ($R = Me, Et$ etc.) generally have geometries of the same type as tris(morpholino)phosphine and tris(piperidino)phosphine.¹

Bond angles around the phosphorus atoms. In I, II and III the sums of the NPN bond angles are 317.7, 317.2 and 318.1°, respectively, which for I and II are 11.1 and 12.2° larger than in tris(morpholino)phosphine and tris(piperidino)phosphine. As in the trivalent species, the NPN bond angles are dissimilar. In I there is one large bond angle, 114.1°, and two smaller ones, 101.2 and 102.4°. In II and III, there are three distinctly different NPN bond angles, 101.0, 105.4 and 110.7° in II, and 101.5, 107.3 and 109.3° in III. In each of the three com-

pounds the largest bond angle is that between bonds to the essentially sp^2 hybridized nitrogen atoms.

It should be emphasized that the sums of the NPN bond angles in all three compounds are significantly less than required for a purely tetrahedral phosphorus atom. The increase in the NPN bond angles relative to those of the trivalent species, on an average of about 4° for each NPN bond angle, does not seem to alter the structure of the molecules significantly, even though the spatial requirements should be better satisfied through increased NPN bond angles. Presumably, owing to the shorter P–N bonds in the pentavalent species than in the trivalent ones, about 0.04 Å (see below), it is equally difficult to accommodate the three substituents in the two classes of compounds.

Bond angles around the nitrogen atoms. As seen from the sum of the bond angles at the nitrogen atoms, $\sum \angle N$, it appears to be three different nitrogen atoms in I and II, whereas in III two of the nitrogen atoms are similar. In I all nitrogen atoms are pyramidally coordinated ($\sum \angle N$ are 340.1, 349.7 and 354.9°); in II one of the nitrogen atoms has a planar coordination and two are pyramidal ($\sum \angle N$ are 343.1, 356.5 and 359.4°); in III the coordination of two nitrogen atoms is nearly planar ($\sum \angle N$ are 342.0, 358.2 and 358.3°). In all the compounds the nitrogen atom with its lone pair direction *anti* to the phosphorus–selenium bond is the one of highest p -character with $\sum \angle N$ in the range 340–343°. As in the trivalent phosphorus species,¹ increased p -character of the nitrogen atom is accompanied by a significant lengthening of the P–N bond.

The phosphorus–nitrogen bond lengths. In tris(morpholino)phosphine and tris(piperidino)phosphine the P–N bond lengths are significantly shorter than the accepted value for a P–N single bond.¹ This shortening has been explained by electron transfer from the phosphorus atom to the nitrogen atom caused by the difference in electronegativity without involving d -orbitals on the central phosphorus atom.^{8,9} The further bond length reduction observed in the pentavalent species, as found in the present study (*cf.* Table 2) and in numerous other investigations,^{10,11} may probably be explained by $p_N \rightarrow d_P$ backbonding since the electronegativity difference between the phosphorus atom and the nitrogen atom in pentavalent species is presumably reversed from trivalent compounds. This backbonding from the nitrogen atoms causes a small but significant decrease in the p -

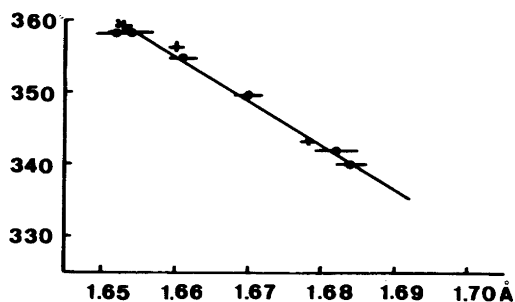


Fig. 2. The P–N bond length vs. the nitrogen bond angle sum in tris(morpholino)phosphine selenide (filled circles), tris(piperidino)phosphine selenide (crosses) and tris(dimethylamino)phosphine selenide (open circles). The e.s.d. in the P–N bonds is indicated.

character of the nitrogen atoms and may be related to the electron donor ability of the amino substituents. It may be noted that the two shorter P–N bonds in the molecules, the bonds in which the d -orbitals on phosphorus may be involved in bonding to the nitrogen atoms, are shorter in II (1.653 and 1.660 Å) and III (1.652 and 1.654 Å) than in I (1.661 and 1.670 Å). As judged by their pK_a -values,¹² piperidine and dimethylamine are considerably better electron donors than is morpholine. The third P–N bond length, which presumably is not influenced by p_x-d_x conjugation, appears to be independent of the electron donating ability of the substituents (1.684 Å in I, 1.678 Å in II and 1.682 Å in III).

Regardless whether d -orbitals on phosphorus are involved in bonding or not, the bond length between phosphorus and nitrogen appears to be closely related to the hybridization of the nitrogen atom. In Fig. 2 the sum of the bond angles around the nitrogen atoms is plotted versus the corresponding P–N bond lengths and a fairly good linear correlation is observed. The slope of the line corresponds approximately to that of the unselenated compounds;¹ it is, however, displaced by 0.04 Å towards shorter bond lengths. Following the argument of Ref. 1 a $P^V-N_{sp^3}$ bond length of 1.70–1.71 Å is thus obtained.

The torsional angles. In Fig. 3 the Newman projections along the P–N bonds are shown. For all three compounds the torsional angle of the P–N bond to the nitrogen atom of highest p -character is close to 180° (see Table 2). The

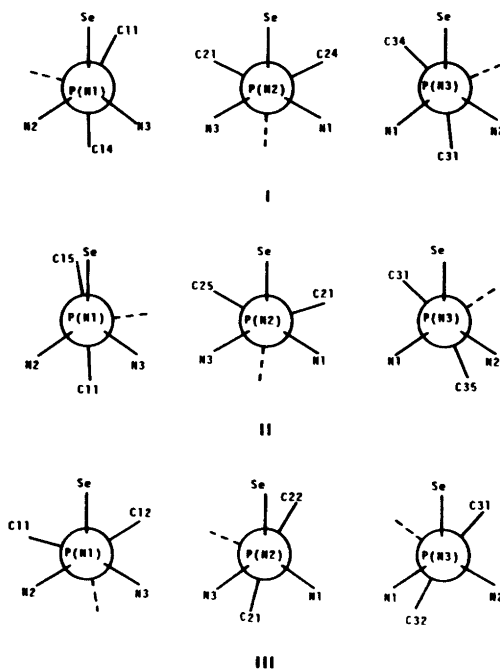


Fig. 3. Newman projections along the P–N bond.

remaining torsional angles are in the range 54–85°, mean value 68° (standard deviation 12°). As in the trivalent species,¹ a torsional angle of 70° appears to be a good compromise between steric repulsion of the atomic cores and the electronic energy.¹⁰ It is notable that in I the two substituents with nitrogen atoms of highest s -character are twisted in opposite directions resulting in a molecule with near m symmetry; this was also found for the unselenated compound.¹ In II, the similarity with the unselenated species, tris(piperidino)phosphine, with regard to the twisting of the substituents is also evident; in these two compounds the two substituents are twisted in the same direction. In III the twisting of the substituents is similar to that in II.

The angles between the P–Se direction and the lone pair directions of the nitrogen atoms are given in Table 3. The lone pair direction is taken as the normal to the plane through three points in unit distance along the bonds from the nitrogen atom.¹ The lone pair of one of the nitrogen atoms is nearly antiparallel to the phosphorus-selenium bond in each of the three compounds; the other two form angles with this bond in the range 59–94°. All

Table 3. Angles (°) between the P–Se direction and the lone pair directions of the nitrogen atoms (for definition, see text).

Angle	I	II	III
P–Se, lone pair N1	81	94	167
P–Se, lone pair N2	170	167	71
P–Se, lone pair N3	71	61	59
Lone pair N1, lone pair N2	107	99	96
Lone pair N1, lone pair N3	80	76	120
Lone pair N2, lone pair N3	115	121	100

nitrogen lone pairs are partly orthogonal to each other in the three compounds.

The structure of the substituents. The morpholino and piperidino substituents in I and II are all in the expected chair conformation and are linked to the phosphorus atom in an approximately equatorial direction. As indicated in Table 2 the bond lengths and also the bond angles in the substituents are significantly dependent on the hybridization of the nitrogen atom. It is noteworthy that the CNC bond angles in the substituents with the nitrogen lone pair antiparallel to the phosphorus–selenium bond are significantly smaller ($1-2^\circ$) than in the remaining two substituents for all three compounds. A detailed discussion of bond lengths and bond angles in the cyclic substituents of I and II will appear in a later paper in this series.

The phosphorus–selenium bond lengths. The observed phosphorus–selenium bond lengths are 2.106(1), 2.1110(4) and 2.120(1) Å, respectively. Since no structure determinations of aminophosphine selenides appear to have been published, an accurate comparison with related compounds is not possible at present. From a recent compilation of P=Se bond lengths,¹³ however, this bond length is known to range from 2.055 Å in 2-seleno-2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane¹⁴ to 2.119 Å in *P*-methyl-*P*-phenylpropylphosphine selenide.¹³ (The very short value of 1.963 Å in triethylphosphine selenide¹⁵ is probably in error; a recent structure determination of trimethylphosphine selenide by electron diffraction has shown the P=Se bond in this compound to be 2.091 Å.¹⁶ On the other hand, the very long P=Se bond observed in tris(2-methylphenyl)phosphine selenide, 2.13 Å,¹⁷ is probably atypical for this class of compounds owing to the steric requirements of the 2-methyl substituents.) The lower limit for the phosphorus–selenium bond thus appears to be

close to 2.07 Å, the value calculated from the covalent double bond radii.¹⁸

The significant elongation of the double bond observed in the present study appears to be caused by a contribution from the dipolar form $\equiv \text{P}^{\delta+} - \text{Se}^{\delta-}$ in the studied compounds.¹⁹ Presumably, due to interaction between the nitrogen atoms and the phosphorus atom, the *d*-orbitals on the phosphorus atom are already engaged in bonding and are not available for bonding with the selenium atom to any significant extent. The results from studies on ⁷⁷Se chemical shifts in various phosphine selenides seem to substantiate this argument.¹⁹ The observation in the present study that II and III, the compounds derived from the more basic amines, contain two nitrogen atoms of higher *s*-character than I, and also have slightly but probably significantly longer phosphorus–selenium bonds than has I, is thus readily understood. The dipolar nature of the phosphorus–selenium bond in tris(dialkylamino)phosphine selenides is exemplified by the powerful electron donor ability towards numerous Lewis acids; see Ref. 20.

The SePN bond angles are in all three compounds significantly different within each compound. The bond angles involving the essentially *sp*³ hybridized nitrogen atoms are 115.1° (I), 115.5° (II) and 114.4° (III) and are from 2 to 4° larger than the remaining SePN angles.

Intramolecular contacts. A number of short non-bonded intramolecular distances are observed. In addition to several normal van der Waals' contacts intramolecular Se–H distances less than 3.0 Å, P–H separations less than 2.9 Å and N–H separations less than 2.5 Å are found and are listed in Table 2.

In all three compounds the selenium atom has a contact to a hydrogen atom from each of the two substituents with *sp*² hybridized nitrogen atoms (2.74–2.91 Å). The phosphorus atom in I and II is in contact with equatorial hydrogen atoms from all carbon atoms bonded to nitrogen (P–H range 2.66–2.87 Å). Corresponding P–H contacts exist in III; in addition there is another P–H contact to each of the methyl groups bonded to N1. In II and III there are N–H nonbonded contacts between the *sp*³ hybridized nitrogen atom (N2 and N1, respectively), and a hydrogen atom of the dialkylamino group corresponding to the smallest Se–P–N-lonepair N torsional angle (N3 in both compounds).

Comments on the potential ambidentate donor ability of tris(dialkylamino)phosphine selenides and

related compounds. The presence of one essentially sp^3 hybridized nitrogen atom in tris(dialkylamino)phosphines¹ and related species²¹ suggests that these compounds may be considered as substituted amines, and the ability of the nitrogen atoms of these compounds to act as electron donors toward certain substrates is well documented.²²⁻²⁵ Similarly, the pentacovalent species derived from tris(dialkylamino)phosphines should in principle exhibit amine functions owing to the presence of one essentially sp^3 hybridized nitrogen atom as shown in the present study.

However, due to the considerable contribution of the dipolar form in tris(dialkylamino)phosphine selenides, and presumably also in the corresponding oxides, $(R_2N)_3PO$, and sulfides, $(R_2N)_3PS$, the nitrogen atoms in this class of compounds can only with difficulty compete with the chalcogenide atoms for Lewis acids.²⁶ Apparently, the nitrogen atoms can only act as the donor when locked in a non-planar configuration, *i.e.* in caged molecules.²⁷ The increased p -character of the nitrogen atoms in these compounds will simultaneously increase the donor ability of the nitrogen atom and reduce the dipolar nature of the phosphorus-chalcogenide bond and thus the donor ability of the chalcogenide atoms. The rather short phosphorus-selenium bond lengths in various substituted 2-seleno-1,3,2-dioxaphosphorinanes¹³ and the weak donor ability of 2-oxo-1,3,2-dioxaphosphorinanes²⁸ suggest that in aminophosphine chalcogenides where the phosphorus atom is a member of a five- or six-membered ring, the donor ability of the chalcogenide atoms may be sufficiently diminished to allow the nitrogen atoms to react with suitable hard Lewis acids. It should be noted that in strongly acidic solutions the chemistry of tris(dialkylamino)phosphine chalcogenides may be governed by initial protonation of the nitrogen atoms. It has recently been shown that the tetra(dimethylamino)phosphonium cation, $(Me_2N)_4P^+$, in presence of concentrated HCl and $SbCl_5$ is transferred into the fairly stable dication $[(Me_2N)_3PMe_2NH]^{2+}$.²⁹

Finally it should be emphasized that the arguments with regard to the structure and reactivity of tris(dialkylamino)phosphines and their chalcogenides may be equally valid for other phosphorus compounds in which the atoms linked to the phosphorus atom have lone pairs of electrons.³⁰ The presence of two electron pairs on each of the neighbouring atoms, however, in trialkylphosphites, $(RO)_3P$, and trithioalkylphosphites, $(RS)_3P$, and in

their pentacovalent chalcogenides will further complicate the problem with regard to the most favourable configuration. The bidentate nature of trialkylphosphates, $(RO)_3PO$, toward certain metal cations³¹ may suggest that one of the alkoxy oxygen atoms is different from the remaining two.

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