

# Structural Studies on the Phosphorus–Nitrogen Bond. VII. The Crystal Structure of *P,P*-Dimorpholinophenylphosphine Selenide and *P,P*-Diphenylmorpholinophosphine Selenide

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The structure of the title compounds,  $[\text{O}(\text{CH}_2\text{-CH}_2)_2\text{N}]_2\text{P}(\text{Se})\text{C}_6\text{H}_5$ , I, and  $\text{O}(\text{CH}_2\text{CH}_2)_2\text{NP}(\text{Se})(\text{C}_6\text{H}_5)_2$ , II, have been determined from X-ray data. Full-matrix least-squares refinements for the non-hydrogen atoms led to final conventional R-values of 0.033 (3849) for I and 0.032 (2087) for II; the number of observed reflections in parentheses. I crystallizes in the monoclinic system with the following unit cell dimensions at 20 °C:  $a=10.266(2)$  Å;  $b=17.286(5)$  Å;  $c=9.706(2)$  Å;  $\beta=112.06(2)^\circ$ . The crystals of II are orthorhombic with cell dimensions at 20 °C:  $a=7.874(2)$  Å;  $b=14.099(2)$  Å;  $c=14.539(2)$  Å. The space groups are  $P2_1/c$  (I) and  $P2_1cn$  (II) and both compounds have four molecules in the unit cell.

The sums of the bond angles at the nitrogen atoms are 342.9 and 348.2° in I and 344.4° in II. In I, the lone pair of the nitrogen atom of highest *p*-character is *antiperiplanar* to the P–Se bond; the lone pair of the other nitrogen atom is roughly orthogonal to the P–Se bond. In II the lone pair of the nitrogen lone pair is strictly *antiperiplanar* to the P–Se bond.

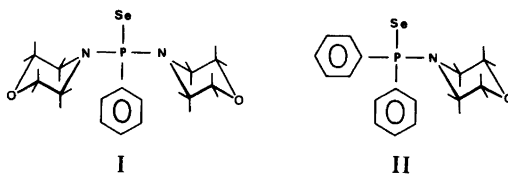
The P–N bond lengths are 1.669(2) and 1.662(2) Å in I and 1.672(4) Å in II. The P–Se bond lengths are 2.097(1) and 2.102(1) Å in I and II, respectively.

In several studies in the present series trivalent and pentavalent phosphorus compounds containing three dialkylamino groups,  $(\text{R}_2\text{N})_3\text{P}$  and  $(\text{R}_2\text{N})_3\text{PX}$ , (X=Se and Te), have been examined by X-ray methods.<sup>1–3</sup> In all the compounds one of the nitrogen atoms is essentially  $sp^3$  hybridized and its lone pair is *anti* to the phosphorus lone pair in the trivalent compounds<sup>1</sup> and to the phosphorus chalcogen bond in the pentavalent compounds.<sup>2,3</sup>

The remaining two nitrogen atoms are generally  $sp^2$  hybridized or close to  $sp^2$  hybridized and their lone pairs are *synclinal* to the phosphorus lone pair or to the chalcogen atom.

In phosphorus compounds containing one or two dialkylamino groups in addition to aryl groups the question arises which conformations of the P–N bonds are the energetically favoured ones. In  $\text{R}'_2\text{PNR}_2$  and in  $\text{R}'_2\text{P}(\text{X})\text{NR}_2$  two conformers are possible when neglecting the various *skew* conformers; the nitrogen lone pair may be *antiperiplanar* or *synclinal* to the phosphorus lone pair or to the X atom. Likewise, with two dialkylamino groups present as in  $\text{R}'\text{P}(\text{NR}_2)_2$  and in  $\text{R}'\text{P}(\text{X})(\text{NR}_2)_2$ , two conformations are conceivable; both the nitrogen lone pairs may be in *synclinal* positions or one of them may be *antiperiplanar* relative to the phosphorus lone pair or to the X atom in the trivalent and in the pentavalent species, respectively.

In an attempt to obtain information with regard to the preferential conformation of the P–N bond in compounds where the phosphorus atom also has aryl substituents, we want to report on the structure of *P,P*-dimorpholinophenylphosphine selenide,  $\text{Mor}_2\text{P}(\text{Se})\text{Ph}$ , I, and *P,P*-diphenylmorpholinophosphine selenide,  $\text{MorP}(\text{Se})\text{Ph}_2$ , II. Admittedly,



the unselenated species of I and II were the compounds of choice; however, owing to difficulties in getting suitable crystals of  $\text{MorPPh}_2$  and its extreme sensitivity to moisture the selenated compounds were chosen. The close similarity between the structure of aminophosphines and their corresponding selenides<sup>1,2</sup> may allow one to draw some conclusions with regard to the structure of  $\text{Mor}_2\text{PPh}$  and  $\text{MorPPh}_2$  from structural studies of I and II.

## EXPERIMENTAL

**Materials.** *P,P*-Dimorpholinophenylphosphine selenide, I, was made from the corresponding phosphine,  $\text{Mor}_2\text{PPh}$ ,<sup>4</sup> 2.8 g, dissolved in 50 ml dry benzene and 1.2 g black selenium powder (50% excess). The mixture was refluxed for 30 min, cooled and filtered, and the product precipitated with light petroleum (40–60°C) at –20°C. After two crystallizations from methanol, 2.6 g, 72%, was obtained, m.p. 121°C (122–124°C<sup>5</sup>). Suitable crystals for the X-ray experiments were grown from a very dilute ethanolic solution by slow cooling to 0°C.

*P,P*-Diphenylmorpholinophosphine selenide, II, was formed by slow addition of 3.5 g, 2 eq., morpholine in 50 ml benzene to 6.0 g, 1 eq., freshly distilled *P*-chlorodiphenylphosphine selenide,  $\text{Ph}_2\text{P}(\text{Se})\text{Cl}$ , dissolved in 100 g benzene. The mixture was stirred for 1 h at room temperature, cooled and filtered, whereupon the solvent was removed *in vacuum*. The oily residue solidified upon addition of cold methanol in which the compound is only slightly soluble. A yield of 3.8 g, 54%, m.p. 118°C, was obtained after two crystallizations from methanol. The crystals from methanol were suitable for the X-ray experiments.

**X-Ray data.** The dimensions of the crystals used were 0.08 × 0.18 × 0.35 mm (I) and 0.30 × 0.30 × 0.50 mm (II). An ENRAF-NONIUS CAD 4 diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation was used for the determination of cell parameters and recording of intensity data. The cell parameters were determined by least squares fits to the diffractometer settings of 25 general reflections for both I and II.  $\text{MoK}\alpha$ -radiation ( $\lambda_{\alpha 1} = 0.70926 \text{ \AA}$ ,  $\lambda_{\alpha 2} = 0.71354 \text{ \AA}$ ) gives reflection peaks with the center of gravity displaced relative to a theoretical center of gravity due to  $\lambda_{\alpha 1}$  alone. The experimentally found centers of gravity were corrected for this offset and the cell parameters were calculated on the basis of  $\lambda_{\alpha 1}$ .

Intensity data were recorded at room temperature (19–20°C) using the  $\omega$ -scan technique with variable scan speed, 0.4–1.5° min<sup>-1</sup> for I and 0.5–3° min<sup>-1</sup> for II. Minimum scan width was 1.5° for both I

and II, including the background scans of 0.25° at the beginning and at the end of the scans. The orientation of the crystals was checked at intervals of 100 recordings. Three standard reflections were remeasured every 2 h and the intensity data later corrected according to the variation of these. Maximum corrections were 6% for I and 3% for II. All crystallographically independent reflections with  $\sin \theta/\lambda < 0.66 \text{ \AA}^{-1}$  were recorded, 3849 for I and 2087 for II. Reflections with  $I < 2\sigma(I)$  were excluded, leaving 2632 reflections for I and 1090 for II.

All computer programs used belong to the ENRAF-NONIUS Structure Determination Pack, version 16, 1979. Atomic form factors and anomalous scattering coefficients were taken from Ref. 6.

## CRYSTAL DATA

I. *P,P*-Dimorpholinophenylphosphine selenide,  $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2\text{PSe}$ , m.p. 121°C. Monoclinic,  $a = 10.266(2) \text{ \AA}$ ;  $b = 17.286(5) \text{ \AA}$ ;  $c = 9.706(2) \text{ \AA}$ ;  $\beta = 112.06(2)^\circ$ ;  $V = 1596.3 \text{ \AA}^3$  (~20°C);  $M = 359.27$ ;  $Z = 4$ ;  $F(000) = 736$ ;  $\mu(\text{MoK}\alpha) = 26.3 \text{ cm}^{-1}$ ;  $D_x = 1.495 \text{ g cm}^{-3}$ . Space group  $P2_1/c$  (No. 14).

II. *P,P*-Diphenylmorpholinophosphine selenide,  $\text{C}_{16}\text{H}_{18}\text{NOPSe}$ , m.p. 118°C. Orthorhombic,  $a = 7.874(2) \text{ \AA}$ ;  $b = 14.099(2) \text{ \AA}$ ;  $c = 14.539(2) \text{ \AA}$ ;  $V = 1614.1 \text{ \AA}^3$  (~20°C);  $M = 350.26$ ;  $Z = 4$ ;  $F(000) = 712$ ;  $\mu(\text{MoK}\alpha) = 26.0 \text{ cm}^{-1}$ ;  $D_x = 1.441 \text{ g cm}^{-3}$ . Space group  $P2_1cn$  (No. 33).

## STRUCTURE DETERMINATIONS

The intensity data were corrected for Lorentz and polarization effects and for absorption. Both structures were solved by interpretation of Patterson and difference Fourier density maps.

From the systematically absent reflections, the space group of II may be  $P2_1cn$  (No. 33) or  $Pmcn$  (No. 62). The choice of the former is justified by the final solution and refinement. The enantiomorph to the presented structure was refined and the result gave unambiguous reason for its exclusion.

Positions for the hydrogen atoms were calculated with a C–H distance of 0.95 Å and fixed; their thermal parameters were refined, averaged and accordingly given the value 5.0 Å<sup>2</sup> and kept fixed in the final refinements. The non-hydrogen atoms were refined anisotropically. The full-matrix least squares refinement program applied minimizes the quantity  $\sum w\Delta F^2$ ; the weights were the inverse of the variance in the observation calculated from

Table 1. Fractional atomic coordinates.

I				II			
ATOM	X	Y	Z	ATOM	X	Y	Z
SE	0.19259(3)	0.45050(2)	0.28192(3)	SE	0.0000(0)	-0.00772(4)	0.15755(4)
P	0.21515(6)	0.56335(4)	0.36694(7)	P	-0.1682(2)	0.0817(1)	0.2288(1)
O1	0.3308(2)	0.5482(1)	0.8599(2)	O	-0.5153(7)	0.2259(3)	0.0283(3)
O2	-0.1600(2)	0.7167(1)	0.1572(3)	N	-0.3112(6)	0.1414(3)	0.1665(3)
N1	0.2595(2)	0.5718(1)	0.5503(2)	C11	-0.4499( 8)	0.0885(4)	0.1223(4)
N2	0.0684(2)	0.6152(1)	0.2985(2)	C12	-0.5812(10)	0.1571(5)	0.0895(5)
C11	0.1508(3)	0.5615(2)	0.6136(3)	C13	-0.5841(10)	0.2749(5)	0.0693(5)
C12	0.2094(3)	0.5899(2)	0.7718(3)	C14	-0.2435(10)	0.2118(4)	0.1010(4)
C13	0.4365(3)	0.5573(2)	0.8002(3)	C21	-0.2990( 7)	0.0201(3)	0.3127(4)
C14	0.3868(3)	0.5280(2)	0.6417(3)	C22	-0.2659( 9)	-0.0737(4)	0.3338(4)
C21	0.0766(3)	0.6985(2)	0.3943(4)	C23	-0.3623(10)	-0.1175(4)	0.4026(4)
C22	-0.0671(3)	0.7294(2)	0.3060(4)	C24	-0.4868(10)	-0.0710(4)	0.4477(4)
C23	-0.1699(3)	0.6366(2)	0.1247(4)	C25	-0.5205(10)	0.0216(4)	0.4260(4)
C24	-0.0303(3)	0.6022(2)	0.1452(3)	C26	-0.4281( 8)	0.0663(4)	0.3589(4)
C31	0.3500(2)	0.6176(1)	0.3325(3)	C31	-0.0616( 7)	0.1770(3)	0.2908(3)
C32	0.3567(3)	0.6134(2)	0.1918(3)	C32	0.1058( 8)	0.1690(4)	0.3149(4)
C33	0.4529(3)	0.6575(2)	0.1584(3)	C33	0.1836( 8)	0.2410(4)	0.3629(4)
C34	0.5463(3)	0.7043(2)	0.2641(3)	C34	0.0963( 8)	0.3202(4)	0.3882(4)
C35	0.5414(3)	0.7085(2)	0.4033(3)	C35	-0.0715( 9)	0.3286(4)	0.3663(4)
C36	0.4425(3)	0.6667(2)	0.4368(3)	C36	-0.1536( 8)	0.2566(4)	0.3179(4)
H111	0.1269	0.5083	0.6114	H111	-0.4992	0.0461	0.1654
H112	0.0695	0.5904	0.5577	H112	-0.4066	0.0537	0.0715
H121	0.1397	0.5841	0.8134	H121	-0.6278	0.1886	0.1414
H122	0.2332	0.6430	0.7722	H122	-0.6682	0.1228	0.0589
H131	0.5175	0.5290	0.8594	H131	-0.4277	0.3082	0.1210
H132	0.4596	0.6106	0.8016	H132	-0.3394	0.3189	0.0262
H141	0.3650	0.4745	0.6393	H141	-0.1585	0.2488	0.1304
H142	0.4586	0.5355	0.6035	H142	-0.1955	0.1800	0.0496
H211	0.1161	0.7253	0.2739	H22	-0.1795	-0.1077	0.3023
H212	0.1344	0.7057	0.4361	H23	-0.3395	-0.1817	0.4180
H221	-0.0605	0.7835	0.3252	H24	-0.5506	-0.1023	0.4941
H222	-0.1036	0.7045	0.3710	H25	-0.6080	0.0548	0.4574
H231	-0.2318	0.6293	0.0244	H26	-0.4532	0.1304	0.3439
H232	-0.2064	0.6109	0.1890	H32	0.1681	0.1139	0.2985
H241	0.0051	0.6258	0.0781	H33	0.3003	0.2353	0.3787
H242	-0.0408	0.5482	0.1261	H34	0.1521	0.3694	0.4211
H32	0.2948	0.5799	0.1187	H35	-0.1326	0.3837	0.3840
H33	0.4546	0.6556	0.0612	H36	-0.2710	0.2618	0.3035
H34	0.6138	0.7336	0.2411				
H35	0.6064	0.7404	0.4770				
H36	0.4378	0.6717	0.5323				

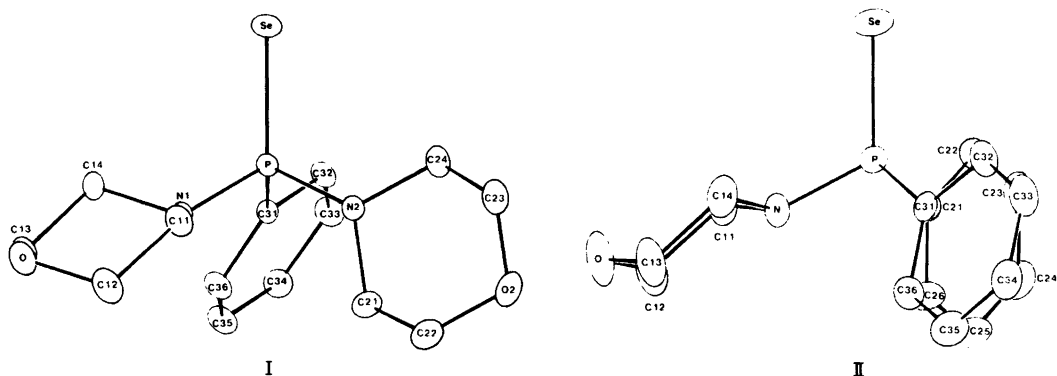


Fig. 1. ORTEP drawings of *P,P*-dimorpholinophenylphosphine selenide (I) and *P,P*-diphenylmorpholino-phosphine selenide (II).

counting statistics plus 2% of the net intensity.

The refinements converged to conventional  $R$  factors of 0.033(I) and 0.032(II); the  $R_w$ -values were 0.033(I) and 0.033(II). The standard deviation of an observation of unit weight,  $[\sum w\Delta F^2/(m-n)]^{1/2}$ , was 1.41 (I) and 1.60 (II).

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

ORTEP drawings of the molecules are shown in Fig. 1 where the numbering of the atoms is included.

Table 2. Structural data.

Bond lengths (Å)

I			II		
P	Se	2.097(1)	P	Se	2.102(1)
P	N1	1.669(2)	P	N	1.672(4)
P	N2	1.662(2)	P	C21	1.817(5)
P	C31	1.805(2)	P	C31	1.822(5)
N1	C11	1.472(3)	N	C11	1.470(6)
C11	C12	1.506(3)	C11	C12	1.494(8)
C12	O1	1.414(3)	C12	O	1.415(8)
O1	C13	1.418(3)	O	C13	1.379(8)
C13	C14	1.515(3)	C13	C14	1.493(9)
C14	N1	1.482(3)	C14	N	1.474(7)
N2	C21	1.475(3)	C21	C22	1.383(6)
C21	C22	1.495(4)	C22	C23	1.399(8)
C22	O2	1.418(3)	C23	C24	1.349(9)
O2	C23	1.415(3)	C24	C25	1.369(7)
C23	C24	1.494(4)	C25	C26	1.371(7)
C24	N2	1.469(3)	C26	C21	1.382(7)
C31	C32	1.395(3)	C31	C32	1.369(6)
C32	C33	1.380(3)	C32	C33	1.376(8)
C33	C34	1.374(3)	C33	C34	1.362(9)
C34	C35	1.372(3)	C34	C35	1.365(8)
C35	C36	1.380(3)	C35	C36	1.394(8)
C36	C31	1.388(3)	C36	C31	1.393(8)
C-H (Assumed)		0.95	C-H (Assumed)		0.95

Table 2. Continued.

## Bond angles (°)

I				II			
Se	P	N1	116.5(1)	Se	P	N	117.3(2)
Se	P	N2	113.3(1)	Se	P	C21	113.7(2)
Se	P	C31	112.9(1)	Se	P	C31	113.3(2)
N1	P	N2	102.8(1)	N	P	C21	102.9(2)
N1	P	C31	103.4(1)	N	P	C31	102.0(2)
N2	P	C31	106.8(1)	C21	P	C31	106.4(2)
P	N1	C11	119.2(1)	P	N	C11	118.8(3)
P	N1	C14	114.8(2)	P	N	C14	116.4(4)
P	N2	C21	118.0(2)	P	C21	C22	120.0(4)
P	N2	C24	120.0(2)	P	C21	C26	121.2(4)
P	C31	C32	118.5(2)	P	C31	C32	120.7(5)
P	C31	C36	123.0(2)	P	C31	C36	119.6(4)
C11	N1	C14	108.9(2)	C11	N	C14	109.1(4)
N1	C11	C12	108.1(2)	N	C11	C12	109.0(4)
C11	C12	O1	112.0(2)	C11	C12	O	113.0(6)
C12	O1	C13	109.4(2)	C11	O	C13	110.2(4)
O1	C13	C14	111.1(2)	O	C13	C14	113.0(5)
C13	C14	N1	108.8(2)	C13	C14	N	109.4(5)
C21	N2	C24	110.2(2)	C26	C21	C22	118.8(4)
N2	C21	C22	109.9(2)	C21	C22	C23	118.6(5)
C21	C22	O2	111.8(2)	C22	C23	C24	121.8(5)
C22	O2	C23	110.1(2)	C23	C24	C25	119.5(5)
O2	C23	C24	112.0(2)	C24	C25	C26	120.0(5)
C23	C24	N2	109.6(2)	C25	C26	C21	121.3(5)
C36	C31	C32	118.4(2)	C36	C31	C32	119.7(6)
C31	C32	C33	120.2(2)	C31	C32	C33	120.0(6)
C32	C33	C34	120.7(2)	C32	C33	C34	121.1(6)
C33	C34	C35	119.6(2)	C33	C34	C35	119.8(6)
C34	C35	C36	120.5(2)	C34	C35	C36	120.3(7)
C35	C36	C31	120.7(2)	C35	C36	C31	119.2(6)

## Various derived and averaged data

	I			II		
	N1	N2	C	N	C21	C31
$\overline{N-C}$ (Å)	1.477	1.472		1.472		
$\overline{C-C}$ (Å)	1.510	1.495	1.382	1.493	1.376	1.377
$\overline{C-O}$ (Å)	1.416	1.417		1.397		
Deviation of N from plane PCC (Å)	0.373	0.309		0.355		
Torsion angle (°):						
Se–P–N-lone pair N	–167.5	–77.7		–177.4		
Se–P–C-ring normal			48.8		–81.9	–69.4
Sum of N bond angles (°)	342.9	348.2		344.4		
Cone angle at P (°)		313.0			311.3	

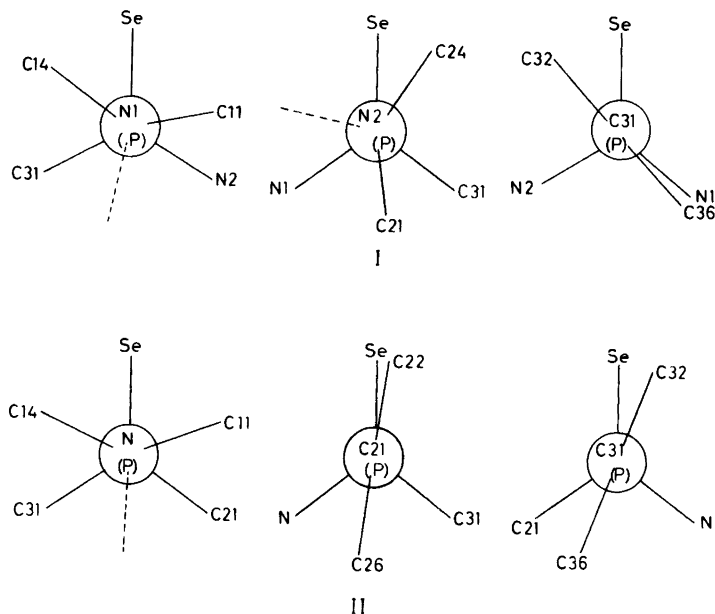


Fig. 2. Newman projections along the P–N and the P–C bonds in *P,P*-dimorpholinophenylphosphine selenide (I) and *P,P*-diphenylmorpholinophosphine selenide (II).

## RESULTS AND DISCUSSION

Bond lengths, bond angles and various other structural data are listed in Table 2. The estimated standard deviations were calculated from the correlation matrices. In Fig. 2 are shown Newman projections of the P–N and P–C bonds where broken lines indicate the nitrogen lone pair directions as defined in Ref. 1. In Table 3 is presented a comparison of pertinent structural parameters in tris(morpholino)phosphine selenide,<sup>1</sup> in I and II from the present study and in triphenylphosphine selenide.<sup>7</sup>

**Conformational considerations.** From NMR studies of acyclic aminophosphines of the general type  $X_2PNR_2$  ( $X = F$  and  $Cl$ ) and related substances there is considerable evidence that the *synclinal* conformation, *i.e.* the lone pairs of the nitrogen and phosphorus atoms being orthogonal, is the best representation of the ground state geometry.<sup>8,9</sup> This observation is in agreement with the so-called “*gauche-effect*”.<sup>10</sup> For the corresponding pentacovalent compounds in solution considerably less is known. NMR experiments are generally far less conclusive owing to the smaller rotational barriers around the  $P^V-N$  bonds combined with

the effect of other exchange processes such as pseudorotation.<sup>11–15</sup> With regard to the preferred conformation of the P–N bond in pentacovalent compounds in the crystalline state, a number of X-ray studies have shown that the nitrogen lone pair is generally orthogonal to the P–X bond; *cf.* Ref. 15 for a survey of references. Furthermore, planarity or near planarity of the bonds to the nitrogen atom is fairly common in aminophosphorus compounds.

In triphenylphosphine<sup>16</sup> and trimesitylphosphine<sup>17</sup> and also in triphenylphosphine oxide<sup>18</sup> the phenyl groups form a propeller-formed arrangement with the normal to the phenyl rings *synclinal* to the phosphorus lone pair or to the oxygen atom. The average torsion angle as defined by normal phenyl-C-P-O (or lone pair P) is about  $55^\circ$  for  $Ph_3P=O$  and  $Ph_3P$  and  $45^\circ$  for  $((CH_3)_3Ph)_3P$ . In the mixed dimethylamino and phenyl phosphine selenides there seems to be a competition of the groups for the *synclinal* conformation and that the phenyl groups have no inclination to take a position where the normal is pointing *antiperiplanar* to the P–Se direction. In both compounds the nitrogen atoms are intermediate between  $sp^2$  and  $sp^2$  hybridized, the sum of the nitrogen bond angles

Table 3. Comparison between some structural parameters in  $\text{Mor}_3\text{PSe}$ ,  $\text{Mor}_2\text{P}(\text{Se})\text{Ph}$ ,  $\text{MorP}(\text{Se})\text{Ph}_2$  and  $\text{Ph}_3\text{PSe}$ .

$\text{Mor}_3\text{PSe}^a$	$\text{Mor}_2\text{P}(\text{Se})\text{Ph}^b$	$\text{MorP}(\text{Se})\text{Ph}_2^b$	$\text{Ph}_3\text{PSe}^c$
<b>P=Se (Å)</b>			
2.106(1)	2.097(1)	2.102(1)	2.106
<b>Cone angle at P (°)</b>			
317.7	313.0	311.3	318
<b>Se–P–N-lone pair N (°)</b>			
–77.6	–77.7		
–178.9	–167.5	–177.5	
65.8			
<b><math>\Sigma \angle \text{N}</math> (°)</b>			
354.9 <i>sc</i> <sup>d</sup>	348.2 <i>sc</i>		
340.1 <i>ap</i> <sup>d</sup>	342.9 <i>ap</i>	344.4 <i>ap</i>	
349.7 <i>sc</i>			
<b>P–N, (P–C) (Å)</b>			
1.659(2) <i>sc</i>	1.662(2) <i>sc</i>	(1.817(5))	
1.681(2) <i>ap</i>	1.669(2) <i>ap</i>	1.672(4) <i>ap</i>	(1.83(1)) <sup>e</sup>
1.668(2) <i>sc</i>	(1.805(2))	(1.822(5))	
<b><math>\angle \text{SePN}</math>, (<math>\angle \text{SePC}</math>) (°)</b>			
112.0 <i>sc</i>	113.3 <i>sc</i>	(113.7)	
115.1 <i>ap</i>	116.5 <i>ap</i>	117.3 <i>ap</i>	(113.1) <sup>e</sup>
111.4 <i>sc</i>	(112.9)	(113.3)	

<sup>a</sup>Ref. 2. <sup>b</sup>This study. <sup>c</sup>Ref. 7. <sup>d</sup>*sc* and *ap* refer to the direction of the nitrogen lone pair being essentially *synclinal* or *antiperiplanar*, respectively, relative to the P=Se bond <sup>e</sup>Average values, cf. Ref. 7.

being 342.9° and 348.2° in I and 344.4° in II. In I the lone pair of the nitrogen atom of highest *p*-character is essentially *antiperiplanar* to the P–Se bond with a torsion angle of –167.5° while the lone pair of the remaining nitrogen atom is approximately *synclinal* to the P–Se bond (torsion angle –77.7°). The torsion angle Se–P–C-ring normal is 48.8°. In II, the lone pair of the one nitrogen atom is strictly *antiperiplanar* with a torsion angle of 177.4°; the Se–P–C-ring normal torsion angles are –81.9 and –69.4°, respectively, cf. Table 2 and Fig. 2.

*The phosphorus–nitrogen bond lengths.* The P–N bond lengths are 1.669 and 1.662 Å in I and 1.672 Å in II. In the previous structural study on several tris(dialkylamino)phosphine selenides, a fairly good linear correlation between the sum of the nitrogen bond angles and the P–N bond lengths was

observed.<sup>2</sup> The P–N bond lengths observed in the present study are slightly but significantly below this line. Apparently, the introduction of phenyl groups into this class of compounds causes a contraction of the P–N bond of approximately 0.01 Å. However, the effect of the phenyl groups does not appear to be additive since the bond length in II, 1.672(4) Å, is quite comparable to the length of the bond linking the phosphorus atom to the one nitrogen atom with its lone pair being *antiperiplanar* to the P–Se bond in I, 1.669(2) Å.

Likewise, there is apparently no significant effect of the number of phenyl groups upon the hybridization of the *antiperiplanar* nitrogen atoms; the sum of the bond angles for these atoms being 342.9 and 344.4° in I and II, respectively. In compounds with three dimethylamino groups,  $(\text{R}_2\text{N})_3\text{PSe}$ , cf.

Ref. 2 and Table 3, the P–N bonds to the *anti-periplanar* nitrogen atoms are significantly longer than the remaining two P–N bonds. In I the two P–N bond lengths are 1.662(2) and 1.669(2) Å, the latter to the nitrogen atom with its lone pair *anti-periplanar* to the P–Se bond. These two bond lengths may not be significantly different; the trend, however, is in accordance with previous findings.<sup>1–3</sup> Presumably the small difference in the hybridization of the two nitrogen atoms in I,  $\Sigma \angle N$  being 342.9 and 348.2°, is the cause for the small or negligible effect upon the observed P–N bond lengths.

*The phosphorus–carbon bond lengths.* The P–C bond length in I may at first sight appear to be slightly shorter than in II, 1.805(2) Å in I and 1.817(5) and 1.822(5) Å in II. However, owing to the lower accuracy in the structural parameters in II, these bond lengths may be equal within the limit of errors. The P–C bond lengths observed in the present study appear to be of the expected magnitude and are possibly slightly longer than that observed in phosphonium salts.<sup>19,20</sup> A further discussion of these bond lengths has to be postponed until sufficient data on P–C<sub>Ar</sub> bond lengths with three reliable digits, as in I, are made available.

In compound II, one of the phenyl rings lies almost parallel to the P–Se bond; the torsion angle Se–P–C–C being only 8.1°, *cf.* Fig. 2. This conformation of one phenyl ring being fairly parallel to the P–X bond appears to be quite common in compounds of the general type Ar<sub>3</sub>PX.<sup>7,18,21,22</sup> Presumably this conformation facilitates an efficient packing of the molecules.

The phenyl rings in both compounds are strictly planar. The angle between the phenyl ring planes in II is 71.6°.

*Bond angles around the phosphorus atom.* The cone angles at phosphorus, 313.0° in I and 311.3° in II, are significantly smaller than both in Mor<sub>3</sub>PSe<sup>2</sup> and in Ph<sub>3</sub>PSe,<sup>7</sup> *cf.* Table 3. Three morpholino substituents and three twisted phenyl groups are thus more space demanding than a mixture of these substituents. Both compounds are fairly asymmetric with regard to the PN<sub>2</sub>C and PNC<sub>2</sub> moieties. In I the angle between the P–C bond and the bond linking the *synclinal* nitrogen atom to the central phosphorus atom is larger than the other NPC angles, 106.8 and 103.4°, respectively. As in Mor<sub>3</sub>PSe, the angle between bonds to *synclinal* and *anti-periplanar* nitrogen atoms is approximately 102°. The CPC bond angle in II, 106.4°, is comparable to the average CPC bond

angle in Ph<sub>3</sub>PSe.<sup>7</sup> It is interesting to note that both I and II are significantly asymmetric with regard to the SePN and SePC bond angles, *cf.* the last entry in Table 3. Apparently, in all compounds studied in this series, the angle between the phosphorus–chalcogen bond and the bond to the nitrogen atom having its lone pair *anti-periplanar* to the P–X bond is 3–4° larger than the remaining two bond angles.<sup>2,3</sup>

*The phosphorus–selenium bond lengths.* P–Se bond lengths in the series Mor<sub>3–n</sub>Ph<sub>n</sub>PSe (*n* = 0, 1, 2 and 3) are highly similar, *cf.* Table 3. Thus, the morpholino group and the phenyl group appear to influence the P–Se bond length to a similar extent. Only in I, *n* = 1, is the P–Se bond slightly but significantly shorter than in the three remaining compounds in the series. The P–Se bond length is known to range from 2.055 Å in 2-seleno-2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane<sup>23</sup> to 2.120 Å in tris(dimethylamino)phosphine selenide.<sup>2</sup> The variations observed are generally regarded to be related to the contribution of the dipolar form  $\equiv P^{\delta+} - Se^{\delta-}$ .

*The morpholino substituents.* These substituents are, in both compounds, in the expected chair conformation and are linked to the phosphorus atom in an approximately equatorial direction. All bond angles and lengths are within the expected range.<sup>1–3</sup> The part of these substituents made up from the four carbon atoms forms strictly a plane within experimental errors. The CNC and the COC planes form angles of 54.0 and 53.6° (N1 ring in I), 50.5 and 52.6° (N2 ring in I) and 51.8 and 50.8° in II with the planes defined by the four carbon atoms. These plane angles in the morpholino rings appear to be related to the hybridization of the nitrogen atoms.

*Intramolecular contacts.* In both I and II the packing in the crystals is of the normal van der Waals' type, the contacts being mainly between hydrogen atoms.

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