

Structural Studies on the Phosphorus-Nitrogen Bond. VIII. The Crystal Structure of Tris(pyrrolidino)phosphine Selenide and Tris(pyrrolidino)phosphine Telluride

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The structures of the title compounds, [(CH₂)₄N]₃PSe, **1**, and [(CH₂)₄N]₃PTe, **2**, have been determined by X-ray counter data. Full-matrix least-squares refinement led to final conventional *R*-factors of 0.066 (4392) for **1** and 0.074 (2290) for **2**. (The number of observed reflections in parentheses).

1 is orthorhombic, space group *P*2₁2₁2₁ with cell dimensions (at -150 °C): *a*=14.715(3) Å, *b*=16.021(4) Å, *c*=12.392(2) Å, *Z*=8. **2** is monoclinic, space group *P*2₁/*n* with cell dimensions (at -150 °C): *a*=13.983(3) Å, *b*=12.249(2) Å, *c*=8.856(1) Å, β=91.31(2), *Z*=4.

In both compounds there exists a disorder in one or more of the five-membered rings. This does not, however, cause any ambiguity with regard to the torsion angles about the P–N bonds. As in previous structure determinations of analogous compounds the conformation of the P–N bond is *anti periplanar* for one amino group and *synclinal* for the two others in each molecule. Owing to the disorder, however, no relationship between the conformation and the P–N bond lengths could be established.

The P–Se bond length in **1** is 2.105(2) Å and 2.107(2) Å for the two non-equivalent molecules, respectively, while the P–Te bond length in **2** is 2.355(3) Å.

In a previous study in this series it was shown that tris(dialkylamino)phosphine tellurides, (R₂N)₃PTe, are readily prepared in high yield from the parent aminophosphines, (R₂N)₃P, and elemental tellurium.¹ In the case of R₂N being morpholino, piperidino and pyrrolidino groups these phosphine tellurides are nicely crystalline

and fairly stable substances. The crystal structure of tris(morpholino)phosphine telluride was presented.¹

A study of the equilibrium constants for the reaction between some trivalent phosphorus compounds and the tellurocyanate ion in acetone at room temperature revealed that tris(dialkylamino)phosphines exert a considerable tellurium basicity in solution, *cf.* eqn. (1).



The equilibrium constants were found to be highly dependent upon the amino groups linked to the phosphorus atom, *K* being ~80 for tris(pyrrolidino)phosphine, 0.60 for tris(piperidino)phosphine and 0.09 for tris(morpholino)phosphine.¹ The exceptional tellurium basicity of the pyrrolidino compound has presumably its origin in the high mesomeric potential of the pyrrolidino group causing this group to be a better donor than all other dialkylamino groups.^{2,3} Pyrr₃P in its ground state may therefore be a better donor than all other tris(dialkylamino)phosphines or, alternative, Pyrr₃PTe is more stable than all other phosphine tellurides due to stabilization of the suggested dipolar form of the phosphorus-tellurium bond caused by the pyrrolidino groups linked to the phosphorus atom. Specific solvent interactions between the trivalent aminophosphines or the pentavalent phosphine tellurides with the solvent molecules, acetone, can hardly be the cause for the large equilibrium constant in the case of Pyrr₃P.

Tris(pyrrolidino)phosphine and its chalcogenides have not been the subject of detailed studies and few data are available to characterize their chemical properties.^{1,4,5} The low χ_i value for the pyrrolidino group as derived from the carbonyl stretching frequency in $\text{Ni}(\text{CO})_3\text{L}$ complexes, L being trivalent phosphorus compounds, suggests Pyrr_3P to be an excellent donor.⁶⁻⁸ Furthermore, the steric demands of phosphines containing pyrrolidino groups are fairly small as viewed by their relatively small Tolman cone angles, θ_i .^{6,9} The considerable contribution of the dipolar form to the P-X bond in the chalcogenides derived from Pyrr_3P is exemplified by the large dipole moment of Pyrr_3PO . This compound has the highest electron donating power of all known aprotic solvents and is superior to other phosphine oxides as complexing agent toward hard metal cations.¹⁰

The stability of Pyrr_3PTe and the remarkable behaviour of Pyrr_3PO as outlined above suggest that the pyrrolidino group interacts differently from other dialkylamino groups with the phosphorus atom. In an attempt to provide some evidence for this suggestion we have turned to structural studies on this class of compounds; to the best of these authors knowledge no X-ray studies on phosphorus compounds containing pyrrolidino groups have been performed. Since Pyrr_3P and Pyrr_3PO are liquids at room temperature and satisfactory crystalline samples could not be obtained at low temperature, the structures of Pyrr_3PSe (1) and of Pyrr_3PTe (2) were determined by X-ray techniques. The close similarity between the structure of aminophosphines¹¹ and their corresponding oxides,¹² selenides¹³ and tellurides¹ may allow one to draw some conclusions with regard to the structure of Pyrr_3P and of Pyrr_3PO from the results of structural studies of 1 and 2. In connection with previous structural studies in this series it was of particular interest to examine whether the observed *synclinal-synclinal-antiperi planar* conformation is retained when the phosphorus atom is linked to the fairly strongly donating pyrrolidino groups.

EXPERIMENTAL

Materials. Pyrr_3PSe (1) and Pyrr_3PTe (2) were prepared and purified as previously described.¹ Suitable crystals for the X-ray study were grown from hexane (argon-flushed n-hexane in the case

of 2). The specimen of 1 was ground to a sphere, diameter 0.4 mm; for 2 a crystal with dimensions $0.1 \times 0.2 \times 0.3$ mm was selected for the structural study.

X-Ray data. Data for the measurements of cell dimensions and intensity data were collected on a SYNTEX P1 diffractometer using graphite crystal monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å). The temperature at the crystal site was -150 °C. Cell parameters were determined by a least squares fit to the diffractometer settings for 15 general reflections with $2\theta > 30^\circ$. Intensities were collected with the $\theta-2\theta$ scan technique; scan speed $2-4^\circ \text{ min}^{-1}$ (2θ) depending on the peak intensity, scan range from 0.9° below $2\theta(a_1)$ to 0.9° above $2\theta(a_2)$ up to a $\sin \theta/\lambda$ limit of 0.8 \AA^{-1} for 1 and 0.6 \AA^{-1} for 2. Background counts were taken for 0.35 times the scan time at each of the scan limits. Three standard reflections were measured at regular intervals during the data collections and the data sets were adjusted according to the systematic variations in their intensities; the maximum correction was 8%. Out of the 4499 unique reflections recorded for 1, 4392 with $I > 2.5 \sigma(I)$ were retained for the structure analysis; the corresponding numbers for 2 were 2749 and 2290. The standard deviations for the intensities were taken as $\sigma(I) = |C_T + (0.02 C_N)^2|^{1/2}$, where C_T is the total number of counts and C_N is the scan count minus background count. The intensities were corrected for Lorentz and polarization effect and, for 1, for absorption.

A description of the computer program applied for the structure determinations is given in Ref. 14. Atomic form factors were those of Doyle and Turner¹⁵ for the heavy atoms and of Stewart, Davidson and Simpson¹⁶ for hydrogen atoms.

CRYSTAL DATA

1. Tris(pyrrolidino)phosphine selenide, $\text{C}_{12}\text{H}_{24}\text{N}_3\text{PSe}$, m.p. 51° (hexane). Orthorhombic, $a = 14.715(3)$ Å, $b = 16.021(4)$ Å, $c = 12.392(2)$ Å, $V = 2921.5$ Å³; ($t = -150$ °C); $M = 320.28$; $Z = 8$; $F(000) = 1328$; $\mu(\text{MoK}\alpha) = 26.6 \text{ cm}^{-1}$; $D_x = 1.456 \text{ g cm}^{-3}$. Absent reflections: ($h00$) for h odd, ($0k0$) for k odd, ($00l$) for l odd. Space group $P2_12_12_1$ (No. 19).

2. Tris(pyrrolidino)phosphine telluride, $\text{C}_{12}\text{H}_{24}\text{N}_3\text{PTe}$, m.p. $84-85$ °C (hexane). Monoclinic, $a = 13.983(3)$ Å, $b = 12.249(2)$ Å, $c = 8.856(1)$ Å, $\beta = 91.31(2)^\circ$, $V = 1516.4$ Å³; ($t = -150$ °C); $M = 368.92$; $Z = 4$; $F(000) = 736$; $\mu(\text{MoK}\alpha) = 21.2 \text{ cm}^{-1}$; $D_x = 1.616 \text{ g cm}^{-3}$. Absent reflections: ($h0l$) for $h+l$ odd, ($0k0$) for k odd. Space group $P2_1/n$ (No. 14).

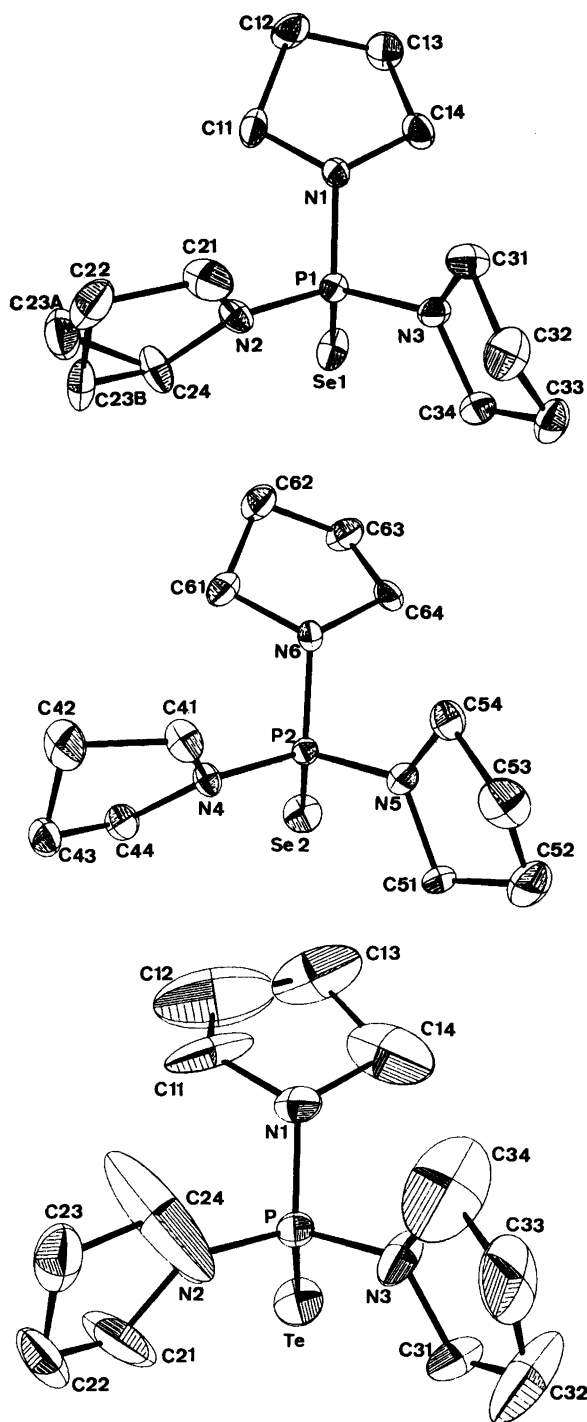


Fig. 1. ORTEP plots of the two non-equivalent molecules in 1 (a and b) and in 2 (c). The ellipsoids are scaled to include 50 % probability.

STRUCTURE DETERMINATIONS

Both structures were solved by the heavy atom Patterson method and refined by successive Fourier syntheses and least squares calculations. Positions were calculated for hydrogen atoms and these were included as fixed contributions with $B=5.0 \text{ \AA}^2$ in the least squares calculations.

In *1*, containing two molecules *per* asymmetric unit, one of the pyrrolidino rings in one of the molecules was found to be disordered. This disorder was treated by splitting one carbon atom (C23) into two parts 0.83 \AA apart with equal statistical weight for each. The refinements con-

verged to a conventional *R*-factor of 0.066, $R_w=0.073$ and $S=|\sum w\Delta F^2/(m-n)|^2=1.76$.

For *2* the disorder is more serious. Several of the carbon atoms were found to have very large thermal motion indicating a pseudorotation in the pyrrolidino moieties. Trials of separating fractional atoms along the long axes of the thermal ellipsoids did not improve the reliability indices, and the structure analysis ended up with planar pyrrolidino rings with unrealistic bond lengths. The final *R*-value was 0.074, $R_w=0.089$ and $S=4.9$.

Final atomic coordinates are listed in Table 1. Tables of observed and calculated structure

Table 1. Fractional atomic coordinates.

Atom	X	¹ Y	Z	Atom	X	² Y	Z
SE1	.33173(5)	.38528(3)	.61738(5)	TE	.76418(6)	-.15520(6)	-.01616(9)
SE2	.34891(5)	.13404(4)	.10746(5)	P	.75626(17)	.03367(22)	.03397(27)
P1	.26298(10)	.34700(8)	.75784(11)	N1	.7605(6)	.0697(7)	.2138(8)
P2	.26894(10)	.13955(8)	.24833(10)	N2	.8461(6)	.1005(7)	-.0388(9)
N1	.3241(3)	.3403(3)	.8695(4)	N3	.6538(7)	.0827(8)	-.0225(13)
N2	.1821(3)	.4131(3)	.7871(4)	C11	.8509(12)	.0606(10)	.2977(14)
N3	.2251(4)	.2498(3)	.7470(4)	C12	.8590(27)	.0078(20)	.4192(30)
N4	.2015(3)	.2208(3)	.2437(4)	C13	.7589(15)	.0084(15)	.4611(30)
N5	.2098(4)	.0537(3)	.2667(4)	C14	.6785(15)	.0404(16)	.3139(23)
N6	.3236(3)	.1434(3)	.3647(3)	C21	.9070(15)	.0718(16)	-.1532(18)
C11	.3581(6)	.4183(4)	.9158(6)	C22	.9546(8)	.1658(11)	-.2118(13)
C12	.4311(5)	.3865(5)	.9965(6)	C23	.9320(9)	.2557(11)	-.1020(14)
C13	.4748(5)	.3136(5)	.9366(7)	C24	.8574(17)	.2179(9)	-.0241(30)
C14	.3975(4)	.2765(4)	.8708(6)	C31	.5995(10)	.0497(11)	-.1577(10)
C21	.1193(5)	.4033(5)	.8819(6)	C32	.5373(12)	.1422(15)	-.2057(23)
C22	.0730(6)	.4884(5)	.8936(7)	C33	.5592(12)	.2331(14)	-.1016(17)
C24	.1654(6)	.4939(4)	.7332(7)	C34	.6144(17)	.1833(10)	.0400(29)
C31	.1866(5)	.2028(4)	.8385(5)				
C32	.0996(6)	.1652(5)	.7891(7)				
C33	.1283(4)	.1446(4)	.6767(6)				
C34	.1891(4)	.2190(4)	.6439(5)				
C41	.1369(4)	.2397(4)	.3323(5)				
C42	.1205(6)	.3342(5)	.3228(6)				
C43	.1294(5)	.3493(4)	.2004(6)				
C44	.2108(5)	.2933(4)	.1695(5)				
C51	.1631(5)	.0131(4)	.1756(5)				
C52	.1070(7)	-.0551(6)	.2258(8)				
C53	.0832(5)	-.0191(6)	.3366(8)				
C54	.1717(5)	.0270(4)	.3694(5)				
C61	.3668(4)	.2293(3)	.3884(5)				
C62	.4437(5)	.2074(4)	.4652(6)				
C63	.4780(5)	.1238(4)	.4209(5)				
C64	.3898(4)	.0786(3)	.3920(5)				
C23A	.1219(15)	.5490(10)	.8208(16)				
C23B	.0812(12)	.5255(9)	.7860(15)				

Table 2. Structural data.

Bond lengths (Å)									
Ia			Ib			2			
Se1	P1	2.105(2)	Se2	P2	2.107(2)	Te	P	2.355(3)	
P1	N1 ^a	1.653(5)	P2	N4	1.639(5)	P	N1 ^a	1.653(9)	
P1	N2	1.633(6)	P2	N5	1.643(6)	P	N2	1.646(9)	
P1	N3	1.660(5)	P2	N6 ^a	1.655(5)	P	N3	1.632(10)	
C-N (average) 1.481(15)					C-N (average) 1.45(4)				
C-C (average) 1.526(20)					C-C (average) 1.48(14)				
P-N (average) 1.647(10)					P-N (average) 1.64(2)				
Angles (°)									
	N1 ^a	N2	N3	N4	N5	N6 ^a	N1 ^a	N2	N3
XPn ($\sigma=0.2^\circ$)	116.7	110.2	111.6	110.0	112.1	116.8	116.4	112.1	110.6
NPN ^b ($\sigma=0.3^\circ$)	112.4	100.9	104.6	101.1	105.8	110.4	111.7	102.0	103.4
$\Sigma\angle N$	343.5	359.6	354.7	358.0	356.7	342.0	348	358	359
X-P-N-Lp(N)	-178.2	85.9	66.6	81.8	58.4	172.6	-177	-80	60
Average bond angles in 1									
\overline{CNC}	110.2(1.1)								
\overline{NCC}	104.0(1.2)								
\overline{CCC}	102.9(0.5)								

^a Nitrogen atom with lone pair *anti* to the P-X bond. ^b The heading Nx is the one not involved in the angle.

factors and of thermal parameters are available from the authors.

ORTEP drawings of the molecules are shown in Fig. 1 where the numbering of the atoms is also indicated. In Table 2 bond lengths, bond angles, torsion angles and other structural data are listed. Estimated standard deviations are calculated from the variance-covariance matrices; in averaged data the numbers in parentheses are standard deviations from the mean.

RESULTS AND DISCUSSION

General structural considerations. As mentioned above disorder was encountered in the present structures. Apparently conformational reorientation takes place in some of the pyrrolidino rings owing to the small energy barriers between the various conformers.¹⁷ According to McCullough and co-workers¹⁸ the barrier to pseudorotation in the pyrrolidine molecule is only some $2.1 \cdot 10^{-21}$ J which is of the same order of magnitude as kT at 120 K, about the tempera-

ture by which the data sets in the present study were collected. Although these compounds may in principle be considered as substituted secondary amines and thus invert^{19,20} and presumably also pseudorotate with less facility than the parent amine, pyrrolidine, more than one conformer may be present even at -150°C . Structural studies on compounds containing unsubstituted pyrrolidono groups should therefore be performed at the lowest possible temperature to avoid significant conformational reorientation to take place; *cf.* the recent study at various temperature of sodium 1-pyrrolidinocarbodithioate dihydrate.²¹

As compared to derivatives of other secondary amines and also of complexes in which secondary amines function as ligands, few structural studies on compounds containing the pyrrolidino group have appeared. The major emphasis seems to have been made on 2-substituted compounds of the proline type, *cf.* Refs. 22-24. Over the last few years some very accurate structure determinations of 1-derivatives of pyrrolidine have

appeared.²⁵⁻³⁰ In all these compounds the nitrogen atom of the pyrrolidino groups is pyramidal. This may suggest that conformational reorientation and thus disorder of the pyrrolidino group will be less frequent the more pyramidal the nitrogen atom is. However, in the case of pyrrolidinium salts,^{28,29} extensive hydrogen bonding may be the cause for the conformational stability at room temperature.

In the structure of **2** the exceptionally large thermal motion of the carbon atoms caused the analysis to yield planar and thus highly unrealistic pyrrolidino groups. The study of **2** may therefore only be considered as an addendum to the study of **1**; the only reliable structural parameters emanating from the study of **2** being the P–Te bond length of satisfactory accuracy together with the TePN and NPN bond angles of modest accuracy, cf. Table 2. However, the study of **2** leaves no doubt with regard to the magnitude of the P–N torsion angles and thus the direction of the nitrogen lone pairs relative to the P–Te direction.

The P–X bond lengths. The P–Se bond length in **1**, 2.105(2) Å and 2.107(2) Å for the two sites, respectively, is not significantly different from the corresponding bond length in Mor₃PSe,¹³ in MorP(Se)Ph₂³¹ and in Ph₃PSe.³² The slightly longer P–Se bond length in Pip₃PSe and in (Me₂N)₃PSe than in Mor₃PSe¹³ suggested a lengthening of this bond with increasing donor ability of the amino groups, presumably due to stabilization of the dipolar form of this bond. However, no further lengthening of the P–Se bond is observed in Pyr₃PSe, the P–Se bond length in this compound is actually somewhat shorter than in Pip₃PSe and in (Me₂N)₃PSe.¹³ We thus have to conclude that no simple relationship exists between the donor ability of the substituents and the P–Se bond length in phosphine selenides.

The P–Te bond length in **2**, 2.355(3) Å, is equal to the corresponding bond length in the morpholino-substituted compound.¹ Thus there is no evidence from the present investigation that the origin for the large tellurium basicity of Pyr₃P is due to an exceptionally strong P–Te bond or to a particularly large contribution of the dipolar form of the P–Te bond. Although the Siebert rule³³ for stretching frequencies for this class of compounds has to be applied with some caution,¹ this conclusion is in agreement with the

previously determined P–X frequencies in (R₂N)₃PSe and (R₂N)₃PTe.¹

The P–N₃ part of the molecules. The usual *sc*, *sc*, *ap* (*gauche-gauche-anti*) conformation as now observed in a number of tris(dialkylamino)phosphines, (R₂N)₃P,¹¹ in their various chalcogenides,^{1,12,13,31} in Mor₃As,³³ and also in the isoelectronic sulfonium salt (R₂N)₃S⁺ BPh₄[–],³⁴ is also found in Pyr₃PSe and Pyr₃PTe. The torsion angles X–P–N–lone pair (N) are, for one of the nitrogen atoms, –178.2 and –172.6° for the two molecules in **1**, respectively, and –177° in **2**. The lone pairs of the remaining two nitrogen atoms are *synclinal* to the P–X bonds; in **1** the torsion angles are about 80° and 60°, in **2** the pyrrolidino groups are twisted in opposite directions and thus have torsion angles of opposite signs. In Fig. 2 are shown Newman projections along the P–N bonds for the two compounds.

The hybridization of the nitrogen atoms in the pyrrolidino groups is described by the sum of the bond angles, Σ∠N°, listed in Table 2. As in numerous compounds previously examined in this series the nitrogen atom with its lone pair direction *antiperiplanar* to the lone pair of the central element in trivalent compounds^{11,23} or to the P–X bond in the pentavalent compounds^{1,12,13,31} has a significantly higher *p*-character than the remaining nitrogen atoms. A fairly linear correlation between the PN bond lengths and Σ∠N° has been observed in the previous studies; unfortunately, the accuracy in the present investigation prevents such a relationship to be established for these two compounds.

In Table 3 a comparison is made between some structural data for various tris(dialkylamino)phosphine selenides and tellurides. It is apparent that the presence of pyrrolidino groups linked to the phosphorus atom causes no distinct changes in the various structural parameters, particularly as compared with piperidino and dimethylamino groups. It is notable that the hybridization of the phosphorus atom, as given by Σ∠NPN°, is independent upon the size and the donor ability of the dialkylamino substituents.

The XPN bond angles are not equal, about 116–117° for the bond angles to the *antiperiplanar* nitrogen atom and 110–112° for the bond angles to the *synclinal* nitrogen atoms in both compounds. This observation is in agreement with previous results on similar compounds.^{1,12,13}

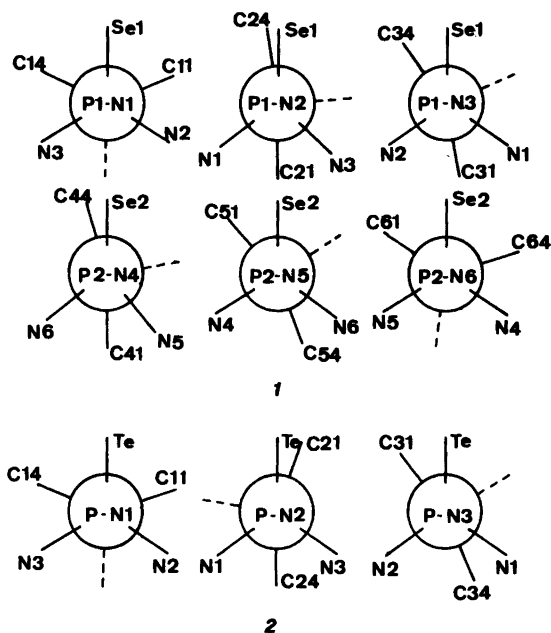


Fig. 2. Newman projections of the P–N bonds. Broken lines indicate the directions of the nitrogen lone pair axes.

The PNC bond angles are also different for those involving the *synclinal* nitrogen atoms, ranging from 116 to 126°. The PNC bond angles involving the *anti* nitrogen atom are fairly similar with a mean of 117(1)°.

The pyrrolidino group. From both theory and experiments it is well known that pyrrolidine and other five-membered ring systems have a highly flexible nature,^{17,35} for a survey of references, *cf.* Ref. 36. Since puckering rotates around the ring without interference from significant energy barriers, none of the conformations of the continuum of possible ones are to be favoured.

No structural conclusions of any value with regard to the pyrrolidino groups can be drawn from the study of 2. In 1 the average CNC bond angle is fairly close to that expected for sp^2 hybridized nitrogen atoms and this bond angle does not seem to be significantly dependent upon the sum of the nitrogen bond angles being 342 or 360°, the extreme values, *cf.* Table 2.

With regard to the conformation of five-membered ring systems attention has generally been focussed on two specific conformations, the envelope form with mirror symmetry and the half-chair form with a two-fold axis. In Table 4 a

Table 3. A comparison between some structural parameters and calculated average parameters in some tris(dialkylamino)phosphine selenides and tellurides.

	P–X(Å)	$\overline{\text{P–N}}(\text{Å})$	$\overline{\Sigma\text{N}^\circ}$	ΣNPN°	Ref.
Pyrr ₃ PSe (1a)	2.105(2)	1.649(14)	352.6	317.9	This study
(1b)	2.107(2)	1.646(8)	352.2	317.3	This study
Mor ₃ PSe	2.106(1)	1.669(11)	348.2	317.7	13
Pip ₃ PSe	2.111(1)	1.662(13)	353.0	317.2	13
(Me ₂ N) ₃ PSe	2.114(1)	1.663(17)	352.8	318.1	13
Pyrr ₃ PTe	2.355(3)	1.644(11)	356	317.1	This study
Mor ₃ PTe	2.356(3)	1.674(11)	347.2	318.3	1

Table 4. The conformation of the pyrrolidino groups in 1.

Ring no.	Conformation	Atom out of plane by four other atoms	Distance from plane (Å)
1	Envelope	C12	+0.57 ^a
2A	Envelope	C23A	+0.42 ^b
2B	Envelope	C23B	-0.40 ^b
3	Envelope	C32	+0.60
4	Envelope	C43	+0.60
5	Half-chair	C52 } C53 }	+0.30 } -0.30 }
6	Envelope	C62	+0.61 ^a

^a Pyrrolidino group with nitrogen atom having lone pair *anti* to the P-Se bond and thus having maximum *sp*³-character (*cf.* text and Table 2). ^b Nitrogen atom is purely *sp*² hybridized and this pyrrolidino group is disordered, *cf.* Table 2 and Fig. 1.

survey is made of the observed conformations of the pyrrolidino groups in 1. In Pyr₃PSe the envelope conformation is apparently the most frequent one; only in ring 5 is the half-chair conformation observed.

In all envelope rings in Pyr₃PSe one of the β-carbon atoms is out of the plane formed by the four other atoms; ring 5 has the half-chair conformation with the β-atoms on each side of the plane formed by the three remaining ring atoms. In compounds with nearly planar nitrogen atoms this flapping of the β-carbon atoms is generally observed. Of 40 proline derivatives examined by De Tar and Luthra only two had a flap involving α-carbon atoms.²⁴

Intermolecular contacts. In neither of the two compounds examined any particularly short intermolecular distances were observed; the contacts seem all to be of normal van der Waals' type.

Conclusions. The structural study of Pyr₃PSe (1) and Pyr₃P₂Te (2) yields no definite conclusion with regard to the exceptional tellurium basicity of Pyr₃P. The similarity in the structure of the morpholino-substituted phosphine chalcogenides, Mor₃PX, and the corresponding pyrrolidino-substituted compounds, 1 and 2, may suggest that the origin to the stability of Pyr₃P₂Te is an exceptionally high donor ability of Pyr₃P. This trivalent phosphorus compound when linked to an electronegative atom as in Pyr₃PO may better satisfy the electronic demands of the oxygen atom than any other trivalent compound. The present results may indicate a possible shortening of the P-N bonds in Pyr₃PSe as

compared to other (R₂N)₃PSe. The P-N bonds in 1 and 2, however, are not exceptionally short as observed for C-N bonds in pyrrolidino-substituted enamines.³⁷

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Received September 8, 1983.