

Structural Studies on the Phosphorus–Nitrogen Bond. III.

The Crystal Structure of Tris(morpholino)phosphine Telluride.

The Tellurium Basicity of Tervalent Phosphorus Species

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The structure of the title compound, $[\text{O}(\text{CH}_2\text{CH}_2)_2\text{-N}]_3\text{PTe}$, has been determined by X-ray methods using diffractometer data. The crystals are monoclinic, space group $P2_1/n$, with (at -151°C) $a=8.735(1)\text{ \AA}$; $b=15.152(2)\text{ \AA}$; $c=12.037(1)\text{ \AA}$ and $\beta=98.30(1)^\circ$. Full-matrix least-squares refinement gave a final R -value of 0.020 for 4336 independent reflections.

The structure of the compound is shown to be very similar to the corresponding selenide. There are two fairly short P–N bonds, 1.66–1.67 Å, and one longer, 1.685(1) Å. As in the selenide and also the parent trivalent phosphorus compound, the nitrogen atom linked to the phosphorus atom through a long bond is essentially sp^3 hybridized and the lone pair of this atom is strictly *anti* to the P–Te bond. The NPN bond angles are highly dissimilar, 114.6, 101.4 and 102.2°; the sum is 318.2° as compared to 317.7° in the selenide. The P–Te bond length is 2.357 Å and the considerable relative elongation as compared to the observed P–Se bond length in the selenide, 2.106(1) Å, is discussed.

Equilibrium constants for the very rapid reactions between the tellurocyanate ion and various trivalent phosphorus compounds have been determined by IR in acetone at room temperature. The equilibrium constants indicate that tris(dialkylamino)phosphines, $(\text{R}_2\text{N})_3\text{P}$, and trialkyl phosphines, R_3P , are superior to other types of trivalent phosphorus species with regard to tellurium basicity. Tris(pyrrolidino)phosphine is exceptionally basic toward tellurium and is the only trivalent phosphorus compound which is significantly more basic than is the cyanide ion. The various possible factors determining the tellurium basicity of trivalent phosphorus species are discussed.

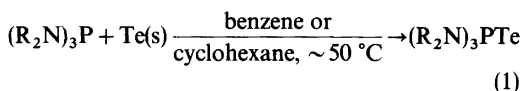
The IR and UV spectra of some tris(dialkylamino)phosphine tellurides and the corresponding selenides are presented.

In Part II of this series the structures of some tris(dialkylamino)phosphine selenides were described.¹ These compounds were shown to be highly asymmetric species which contained at least two different nitrogen atoms, two different P–N bond lengths and two different NPN angles. Apart from the cone angle at phosphorus and somewhat shorter P–N bonds these compounds were found to be structurally quite similar to the previously investigated tris(dialkylamino)phosphines.²

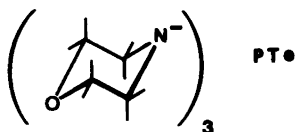
During the synthesis of the tris(dialkylamino)phosphine selenides from the aminophosphines and elemental selenium powder it was noted that these reactions, even when performed in lukewarm benzene or cyclohexane, were fairly rapid, in contrast to what is the case when selenophosphates and triaryl phosphine selenides are formed from elemental selenium and trialkyl phosphites and triaryl phosphines, respectively.^{3,4} Furthermore, the aminophosphine selenides are very stable and can be crystallized from a number of solvents even at elevated temperatures and can be stored for long periods in sunlight without the pink colorization due to selenium, which is so typical for many phosphine selenides derived from other trivalent phosphorus species. Apparently, tris(dialkylamino)phosphines are more basic toward selenium than are other trivalent phosphorus species, presumably owing to the structural arrangement of the three

nitrogen atoms around the phosphorus atom in $(R_2N)_3P$.²

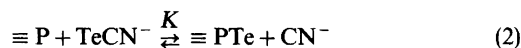
In order to gain further information on structures of tris(dialkylamino)phosphines and their chalcogenides, we have turned to the tellurides, $(R_2N)_3P\text{Te}$. Once more it was observed that tris(dialkylamino)phosphines act exceptionally; the tellurides are formed rapidly in high yield, especially when aminophosphines derived from cyclic secondary amines are employed; eqn. (1), where R_2N = morpholino (Mor), piperidino (Pip) or pyrrolidino (Pyr). Furthermore, these aminophosphine



tellurides, in contrast to tellurides derived from $(Me_2N)_3P$ ^{5,6} and $(Et_2N)_3P$,⁷ are stable and nicely crystalline compounds which can be crystallized from a number of solvents, protic or aprotic, polar or nonpolar, provided the temperature during the dissolution is kept below $\sim 50^\circ\text{C}$. The compounds may be stored for long periods and oxygen does not seem to increase their rate of decomposition, neither in solution nor in the solid state.⁵ In this study we want to report the crystal and molecular structure of one of the synthesized tellurides, tris(morpholino)phosphine telluride, Mor_3PTe . During the progress of this study the first structural report of a compound with a P–Te bond appeared.^{8,9}



Tris(dialkylamino)phosphines have been found to react very rapidly with the tellurocyanate ion, TeCN^- , in acetone. These reactions, however, are not quantitative and equilibria are established, eqn. (2).



By employing various trivalent phosphorus compounds, their tellurium basicity relative to the cyanide ion can be determined from the equilibrium constants. Detellurization reactions and equilibria involving the tellurium atom, are most rare in the literature,^{10,11} in contrast to deselenation reac-

tions.¹² Further knowledge of the various factors determining the stability of phosphine tellurides may prove to be of importance when these compounds are to be applied in deoxygenation reactions¹³ and, if possible, as ligands in coordination chemistry.¹⁴

EXPERIMENTAL

Solvents. Acetone, Merck *p.a.*, was treated with potassium carbonate and distilled in an argon atmosphere. Acetonitrile, Baker Analyzed Reagent, was distilled from phosphorus pentoxide and finally from calcium hydride in an argon atmosphere prior to use. Methanol, Merck *p.a.*, was used without further purification. Benzene, cyclohexane, diethyl ether, hexane and pentane were treated with metallic sodium and flushed with dry argon.

Materials. Tris(dialkylamino)phosphines, $(R_2N)_3P$. These compounds were prepared according to standard procedures from 1 mol phosphorus trichloride and 6 mol dialkylamine, freshly distilled from potassium hydroxide, in benzene or diethyl ether. The crude products were dissolved in benzene or diethyl ether and were repeatedly treated with small portions of ice-water until the test for ionic chloride was negative. The liquid aminophosphines were purified by distillation under reduced pressure, Pip_3P and Mor_3P by sublimation and crystallization, respectively, as reported.²

Trialkylphosphites, $(RO)_3P$. The commercial compounds were first distilled, then dissolved in a large volume of diethyl ether, >10:1, and treated with metallic sodium overnight. After filtration the compounds were twice distilled in vacuum. The tris(dialkylamino)phosphines and the trialkyl phosphites were carefully shielded from atmospheric moisture.

Tributyl phosphine, Bu_3P , was twice distilled in an argon atmosphere at reduced pressure. Triphenyl phosphine, Ph_3P , and P,P-dimorpholino-phenyl phosphine, Mor_2PPh , were purified as described.³

Bis(triphenylphosphine)iminium tellurocyanate and cyanide, $[\text{PNP}]^+\text{TeCN}^-$ and $[\text{PNP}]^+\text{CN}^-$, were prepared and purified as reported.¹⁵

Tris(morpholino)phosphine telluride, Mor_3PTe . To 3.2 g tris(morpholino)phosphine in 25 ml benzene was added 3 g black tellurium powder and the mixture kept at $50-60^\circ\text{C}$ under constant stirring for 30 min. After filtration the solvent was removed in vacuum and the residue twice crystallized from luke-warm methanol. Yield of cream-yellow crystals, 2.9 g, 63%, m.p. $130-132^\circ\text{C}$ (dec). This compound could also be crystallized from luke-warm cyclohexane, hexane and from refluxing pentane. In benzene and acetonitrile the compound slowly decomposes at room temperature.

Tris(piperidino)phosphine telluride, Pip_3PTe , and tris(pyrrolidino)phosphine telluride, Pyrr_3PTe , were prepared in a similar manner, but in cyclohexane or hexane as solvent. These compounds were finally obtained in 60–80% yield after two crystallizations from hexane. Both compounds are slightly cream-yellow crystalline substances, Pip_3PTe m.p. 94–95 °C (dec) and Pyrr_3PTe m.p. 84–85 °C (dec).

Tris(pyrrolidino)phosphine selenide, Pyrr_3PSe , m.p. 51 °C (hexane), apparently a new compound, was prepared in close to quantitative yield from the parent aminophosphine and elemental selenium in cyclohexane at room temperature. Mor_3PSe and Pip_3PSe , were prepared and purified as reported.¹

X-Ray data. Crystals of tris(morpholino)phosphine telluride, Mor_3PTe , suitable for the X-ray study were grown from methanol. The crystal used for the X-ray experiments was of approximately spherical shape, diameter 0.35 mm. Data were collected on a SYNTEX PI diffractometer with –151 °C at the crystal site, using graphite crystal monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71069$ Å). Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Intensity data were recorded with the $\theta-2\theta$ scan technique, scan speed (2θ) was 3° min⁻¹, scan width 1.5°. All intensities in a quadrant of reciprocal space within $\sin \theta/\lambda=0.7$ Å⁻¹ were measured; background counts were taken at each of the scan limits for 0.35 times the scan time. Three standard reflections were measured after every 100 reflections, variations of up to 1.5% in the intensities were observed and the data were accordingly adjusted. Of the 4876 independent reflections measured 4336 with $I>2.5\sigma(I)$ were retained for the structure determination. 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 analysis is given in Ref. 16. Atomic scattering factors were taken from Ref. 17 for Te, Ref. 18 for P, O, N and C, and Ref. 19 for H.

Determination of equilibrium constants according to eqn. (2). The amount of consumed or formed ionic tellurocyanate, TeCN^- , was determined by IR at 2081 cm⁻¹. By employing liquid cells of 0.1 cm path length the concentration of ionic tellurocyanate could be determined with an accuracy of $\pm 2\%$ in the $3-15 \times 10^{-3}$ M range. For reactions between ionic tellurocyanate and trivalent phosphorus compounds the initial concentration of ionic tellurocyanate was usually in the $10-15 \times 10^{-3}$ M range and the concentration of the phosphorus compound so chosen, when experimentally possible, that 30 to 70% of the tellurocyanate ion was con-

sumed. By this procedure the equilibrium constant could be determined with an accuracy of $\pm 10\%$.

For the most weakly basic phosphorus compounds, *i.e.* the trialkyl phosphites, $(\text{RO})_3\text{P}$, and Mor_2PPh , this reduction in the concentration of the tellurocyanate ion could not be achieved, even when the concentration of the trivalent phosphorus compounds was 10 to 20 times that of the tellurocyanate ion, 0.1 to 0.3 M. The equilibrium constants involving these phosphorus donors could thus only be determined with highly limited accuracy. Control experiments showed that the tellurocyanate ion and the cyanide ion did not attack the alkyl groups in the trialkylphosphites.

The equilibrium constant for the reaction between tris(pyrrolidino)phosphine, Pyrr_3P , and the tellurocyanate ion could only be determined from the reverse reaction between the phosphine telluride and ionic cyanide in large excess owing to the exceptionally high tellurium basicity of Pyrr_3P . Pyrr_3P appeared fairly unstable in both acetone and acetonitrile preventing stock solutions of the compound to be made.

All equilibrium constants determined in the present study were determined by at least three different concentrations of each of the reactants and the solutions were made by separate weighings. To avoid experimental difficulties due to oxidation of the tellurocyanate ion²⁰ and the cyanide ion²¹ all solutions of salts of these ions were carefully shielded from atmospheric oxygen. The equilibrium experiments were performed at 22 ± 2 °C and a Perkin-Elmer 399 B Infrared Spectrophotometer was employed. The IR spectra of the solid compounds were determined by the KBr-mull technique.

The UV spectra of Mor_3PX ($X=\text{O}, \text{S}, \text{Se}$ and Te), Pip_3PTe and Pyrr_3PTe were determined in methanol, while the spectrum of Mor_3P was measured in cyclohexane. A Perkin-Elmer UV-VIS Spectrophotometer Model 555 was employed.

CRYSTAL DATA

Tris(morpholino)phosphine telluride, $\text{C}_{12}\text{H}_{24}\text{N}_3\text{O}_3\text{PTe}$, m.p. 130–132 °C (dec). Monoclinic, $a=8.735(1)$ Å; $b=15.152(2)$ Å; $c=12.037(1)$ Å; $\beta=98.30(1)^\circ$; $V=1576.4$ Å³ ($t=-151$ °C). $M=416.93$; $Z=4$; $F(000)=832$; $\mu(\text{MoK}\alpha)=20.7$ cm⁻¹; $D_x=1.757$ g cm⁻³. Space group $P2_1/n$ (No. 14).

STRUCTURE DETERMINATION

The structure was determined by Patterson methods followed by successive Fourier syntheses. Refinement was performed as described in Refs. 1 and 2; it converged to a conventional *R*-factor of

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	.06088(1)	.21858(1)	.17376(1)	.0158(1)	.0152(1)	.0173(1)	.0041(0)	.0004(0)	-.0011(0)
P	.28296(4)	.13126(2)	.22534(3)	.0116(1)	.0091(1)	.0086(1)	.0002(1)	.0013(1)	-.0002(1)
O1	.3272(1)	-.0870(1)	-.0230(1)	.0238(5)	.0170(5)	.0143(5)	.0033(4)	.0039(4)	-.0041(4)
O2	.7181(1)	.2954(1)	.2868(1)	.0144(4)	.0164(5)	.0219(5)	-.0020(4)	.0028(4)	.0039(4)
O3	.2043(1)	.0233(1)	.5609(1)	.0187(5)	.0181(5)	.0117(4)	-.0046(4)	.0055(4)	-.0016(4)
N1	.2859(1)	.0449(1)	.1389(1)	.0179(5)	.0121(5)	.0096(5)	.0023(4)	.0021(4)	-.0007(4)
N2	.4453(1)	.1902(1)	.2444(1)	.0141(5)	.0123(5)	.0141(5)	-.0004(4)	.0009(4)	.0036(4)
N3	.2875(1)	.0806(1)	.3503(1)	.0148(5)	.0120(5)	.0098(5)	-.0019(4)	.0026(4)	-.0009(4)
C11	.4011(2)	-.0267(1)	.1644(1)	.0196(6)	.0133(6)	.0133(6)	.0034(5)	.0034(5)	-.0001(4)
C12	.3475(2)	-.1072(1)	.0938(1)	.0938(1)	.0125(6)	.0164(6)	-.0000(5)	.0076(5)	-.0002(5)
C13	.2128(2)	-.0198(1)	-.0471(1)	.0232(7)	.0218(7)	.0151(6)	.0036(5)	-.0004(5)	-.0065(5)
C14	.2596(2)	.0640(1)	.0172(1)	.0224(6)	.0160(6)	.0097(5)	.0033(5)	.0024(5)	-.0002(5)
C21	.5979(2)	.1494(1)	.2810(1)	.0145(6)	.0134(6)	.0159(6)	.0013(5)	.0023(5)	.0019(5)
C22	.7033(2)	.2159(1)	.3488(1)	.0147(6)	.0167(6)	.0169(6)	-.0010(5)	.0009(5)	.0025(5)
C23	.5703(2)	.3340(1)	.2529(1)	.0169(6)	.0132(6)	.0218(6)	-.0000(5)	.0030(5)	.0033(5)
C24	.4627(2)	.2714(1)	.1801(1)	.0197(6)	.0160(6)	.0160(6)	-.0026(5)	.0008(5)	.0064(5)
C31	.1606(2)	.0167(1)	.3561(1)	.0160(6)	.0150(6)	.0119(6)	-.0040(5)	.0028(5)	-.0008(4)
C32	.1909(2)	-.0342(1)	.4658(1)	.0193(6)	.0134(6)	.0129(6)	-.0023(5)	.0049(5)	-.0007(5)
C33	.3267(2)	.0855(1)	.5557(1)	.0172(6)	.0189(6)	.0119(6)	-.0041(5)	.0031(5)	-.0024(5)
C34	.2995(2)	.1400(1)	.4487(1)	.0192(6)	.0133(6)	.0113(5)	-.0027(5)	.0039(5)	-.0028(4)

Atom	x	y	z	B	Atom	x	y	z	B
H111	.414	-.042	.246	1.3	H112	.496	-.011	.150	1.3
H121	.257	-.127	.111	1.4	H122	.424	-.151	.103	1.4
H131	.104	-.043	-.027	1.4	H132	.190	-.006	-.130	1.4
H141	.177	.104	.004	1.3	H142	.351	.089	-.007	1.3
H211	.646	.130	.212	1.3	H212	.581	.100	.324	1.3
H221	.806	.190	.363	1.4	H222	.671	.234	.427	1.4
H231	.596	.389	.210	1.4	H232	.514	.347	.314	1.4
H241	.512	.256	.115	1.3	H242	.357	.296	.159	1.3
H311	.159	-.028	.285	1.3	H312	.050	.046	.349	1.3
H321	.289	-.069	.466	1.4	H322	.104	-.073	.469	1.4
H331	.426	.054	.555	1.4	H332	.322	.125	.618	1.4
H341	.385	.182	.452	1.3	H342	.209	.174	.446	1.3

0.020, R_w of 0.025 and an S -value, $[\sum w\Delta F^2/(m-n)]^{1/2}$, of 1.66; the overdetermination ratio was 13.8.

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

Analysis of the rigid body vibrations were carried out, both for the molecule as a whole and for the separate morpholino substituents. For the discussion of the structure bond lengths corrected for librations are used.

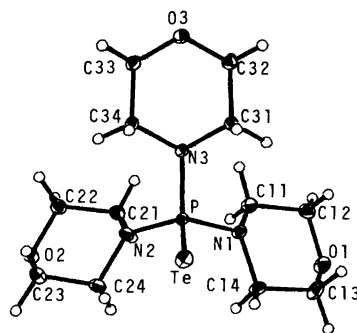


Fig. 1. ORTEP drawing of tris(morpholino)phosphine telluride.

Table 2. Structural data for tris(morpholino)phosphine telluride.

Bond lengths (Å)				Corr.	Bond angles (°)			
P	Te	2.3561(3)	2.3571	Te	P	N1	111.17(4)	
P	N1	1.674(1)	1.675	Te	P	N2	112.82(4)	
P	N2	1.664(1)	1.664	Te	P	N3	113.81(4)	
P	N3	1.685(1)	1.685	N1	P	N2	114.57(6)	
N1	C11	1.481(2)	1.482	N1	P	N3	101.44(6)	
C11	C12	1.523(2)	1.524	N2	P	N3	102.24(6)	
C12	O1	1.424(2)	1.426	P	N1	C11	121.0(1)	
O1	C13	1.426(2)	1.428	P	N1	C14	116.7(1)	
C13	C14	1.512(2)	1.513	N1	C11	C12	109.0(1)	
C14	N1	1.478(2)	1.480	C11	C12	O1	111.3(1)	
N2	C21	1.478(2)	1.479	C12	O1	C13	109.8(1)	
C21	C22	1.520(2)	1.521	O1	C13	C14	111.4(1)	
C22	O2	1.432(2)	1.432	C13	C14	N1	109.6(1)	
O2	C23	1.422(2)	1.422	C14	N1	C11	110.7(1)	
C23	C24	1.521(2)	1.521	P	N2	C21	122.1(1)	
C24	N2	1.472(2)	1.472	P	N2	C24	121.8(1)	
N3	C31	1.481(2)	1.481	N2	C21	C22	109.4(1)	
C31	C32	1.519(2)	1.520	C21	C22	O2	111.8(1)	
C32	O3	1.430(2)	1.431	C22	O2	C23	110.4(1)	
O3	C33	1.434(2)	1.434	O2	C23	C24	111.7(1)	
C33	C34	1.520(2)	1.520	C23	C24	N2	108.7(1)	
C34	N3	1.480(2)	1.484	C24	N2	C21	110.5(1)	
Torsion angles (°)				P	N3	C31	114.7(1)	
Te	P	N1	C11	P	N3	C34	115.3(1)	
Te	P	N1	C14	N3	C31	C32	109.6(1)	
Te	P	N2	C21	C31	C32	O3	111.8(1)	
Te	P	N2	C24	C32	O3	C33	109.9(1)	
Te	P	N3	C31	O3	C33	C34	111.6(1)	
Te	P	N3	C34	C33	C34	N3	109.4(1)	
N1	P	N2	C21	C34	N3	C31	109.2(1)	
N1	P	N2	C24					
N1	P	N3	C31					
N1	P	N3	C34					
N2	P	N3	C31					
N2	P	N3	C34					
N2	P	N1	C11					
N2	P	N1	C14					
N3	P	N1	C11					
N3	P	N1	C14					
N3	P	N2	C21					
N3	P	N2	C24					
Various derived and averaged data								
Nx				N1	N2	N3		
N–C (Å)				1.481	1.476	1.483		
C–C (Å)				1.519	1.521	1.520		
C–O (Å)				1.427	1.427	1.433		
Deviation of Nx from plane PCC (Å)				0.31	0.21	0.41		
Sums of Nx bond angles (°)				348.3	354.3	339.2		
Torsion angle Se–P–N–Lone pair (N) (°)				–60.4	73.2	178.5		
Sum of NPN angles (°)					318.3			

Table 3. A comparison between some structural parameters in tris(morpholino)phosphine, Mor_3P , tris(morpholino)phosphine selenide, Mor_3PSe and tris(morpholino)phosphine telluride, Mor_3PTe .

	Mor_3P			Mor_3PSe			Mor_3PTe		
	N1^a	N3	N2^b	N2^a	N3	N1^b	N3^a	N1	N2^b
$\Sigma \angle \text{N}^\circ$	337.6	350.5	353.2	340.1	349.7	354.9	339.2	348.3	354.3
Torsion angle	170.6	-73.2	70.9	-178.9	65.8	-77.6	178.5	-60.4	73.2
$\text{P}-\text{N}$ (Å) corr.	1.726(3)	1.696(3)	1.691(3)	1.684(2)	1.670(2)	1.661(2)	1.685(1)	1.675(1)	1.664(1)
$\Sigma \angle \text{NPN}^\circ$		306.6			317.7			318.3	
$\Sigma \text{P}-\text{N}$ (Å)		5.113			5.015			5.024	
$\text{P}-\text{X}$ (Å)					2.106(1)			2.3571(3)	

^a The nitrogen atom with its lone pair *anti* to the phosphorus lone pair or the $\text{P}-\text{X}$ bond ($\text{X}=\text{Se}, \text{Te}$). ^b The nitrogen atom with lone pair of lowest *p*-character.

RESULTS AND DISCUSSION

An ORTEP drawing of the molecule is shown in Fig. 1 where the numbering of the atoms is also indicated. A list of bond lengths and bond angles, torsion angles and other structural data is given in Table 2. Estimated standard deviations are calculated from the correlation matrix.

General remarks. In Table 3 are collected some important structural parameters in tris(morpholino)phosphine,² Mor_3P , in tris(morpholino)phosphine selenide,¹ Mor_3PSe , and in the corresponding telluride, Mor_3PTe , determined in the present study.

The results in Table 3 clearly indicate that the telluride is, with regard to the PN_3 moiety, structurally very similar to the selenide. The $\text{P}-\text{N}$ bond lengths, the sum of the nitrogen bond angles, $\Sigma \angle \text{N}$, and the sum of the NPN bond angles, $\Sigma \angle \text{NPN}$, are, within experimental error, identical in the telluride and in the selenide. Apparently, the phosphorus-tellurium bond exerts the same conformational influence as does the phosphorus-selenium bond¹ and the lone pair² when the phosphorus atom is linked to three nitrogen atoms. As a result, the lone pair of the nitrogen atom of highest *p*-character, is anti-parallel to the phosphorus-tellurium bond, similar to what is the case in the selenide. The similarity in the $\text{P}-\text{N}$ bond length and the sum of the nitrogen bond angles in the telluride and in the selenide do not indicate any significant difference in the hybridization of the phosphorus atoms in the two compounds.

With regard to the torsion angles involving the nitrogen atoms not having their lone pair anti-

parallel to the phosphorus-chalcogen bond, a slight difference between the telluride and the selenide is observed, Table 3. (For definition of torsion angles, Ref. 2). Presumably, this is due to the hydrogen atoms at C14 and C24, which will tend to be at van der Waals distance from the larger tellurium atom. The reduction in torsion angles, 65.8 and 77.6° in the selenide to 60.4° and 73.2° in the telluride, is in the expected direction. The structure of the morpholino substituents in the telluride and the selenide is equal within the experimental error.

The phosphorus-tellurium bond length. The observed phosphorus-tellurium bond length is 2.3571(3) Å. This bond length is comparable with the one observed in 1,3-dimethyl-2-telluro-2-*cis*-4-bis(*tert*-butyl)-1,3,2λ⁵,4λ³-diazadiphosphetidine, 2.354(7) Å,⁸ and 2.327(2) Å and 2.305(5) Å in the corresponding *trans*-ditelluride and *cis*-ditelluride, respectively.⁹ In the monotellurated diazaphosphetidine^{8,22} and in the *cis*-ditellurated compound,⁹ the two nitrogen atoms linking the two phosphorus atoms in the four-membered ring are intermediate between *sp*² and *sp*³ hybridized as are the nitrogen atoms in the present compound, tris(morpholino)phosphine telluride, *cf.* Table 3. In the *trans*-ditellurated diazaphosphetidine⁹ the coordination of the two nitrogen atoms is essentially planar. In none of the studied tellurated diazaphosphetidines are there any close intermolecular contacts between the tellurium atoms and neighbouring phosphorus atoms as observed in the adduct between triphenylphosphine telluride and triphenylphosphine.²³ Likewise, there are no close contacts between the tel-

lurium atoms and phosphorus atoms in Mor_3PTe ; the shortest Te–O distance in the present compound is 3.65 Å as compared with a van der Waals distance of 3.60 Å. Since there appear to be no quasi-linear P–Te⋯O or P–Te⋯N bonding arrangements of the type observed in 2-substituted phenyltellurenyl halides,²⁴ the observed P–Te bond lengths are to be considered as true bond lengths and are presumably typical for this class of compounds.

The P–Te bond length of 2.3571(3) Å, as observed in the present study, is intermediate between a P–Te single bond, 2.48 Å, and a double bond, 2.27 Å.²⁵ The considerable elongation from the observed P–Se bond length in the corresponding selenide, 2.106(1) Å,¹ 0.251 Å, even though the difference between the double bond radii of Se and Te is only 0.20 Å, suggests that the the dipolar form, $\text{P}^{\delta+}\cdots\text{X}^{\delta-}$, contributes more to the P–Te bond than to the P–Se bond. Dipole moment studies on phosphine chalcogenides have shown that the polarity increases in the series oxide < sulfide < selenide.²⁶ However, the results from the only dipole study of pentavalent phosphorus compounds in which the telluride is included, tri-*n*-octylphosphine chalcogenides, do not confirm that the telluride is more polar than is the selenide. Apparently, dipole studies of phosphine chalcogenides or tris(dialkylamino)phosphine chalcogenides with smaller alkyl groups are necessary for a definite proof. Toward a soft acid like iodine the donor ability of phosphine chalcogenides increases in the order oxide < sulfide << selenide.²⁸ The observation that tris(dimethylamino)phosphine telluride, presumably a very soft donor, is an equally good donor as is the corresponding selenide toward phenol,²⁹ a hard acid, and a considerably better donor toward sulfur dioxide than is the selenide⁶ may prove as evidence for the suggestion that the polar nature of the P–Te bond is superior to that of the P–Se bond in corresponding compounds.

It is notable that the observed elongation of the P–X bond from the bond length in the selenide¹ to the bond length in the telluride is not accompanied by any significant decrease in the P–N bond lengths or increase in the *s*-character of the nitrogen atoms, *cf.* Table 3. This observation may suggest that the cause for the increased dipolar nature of the telluride is not due to the nitrogen atoms. Presumably, the large difference in size between the tellurium atom and the phosphorus atom will efficiently hinder a sufficient overlap of these atom's orbitals and thus generate a bond of

Table 4. Equilibrium constants for the reactions between some trivalent phosphorus compounds and the tellurocyanate ion in acetone at ambient temperature.

$$K = \frac{[\equiv\text{PTe}][\text{CN}^-]}{[\text{TeCN}^-][\equiv\text{P}]}$$

Tervalent P-compounds	K ^a
Pyrr ₃ P	80 ^b (~ 140 in MeCN)
CN ⁻	1 (definition)
Pip ₃ P	0.60 ^b
(Me ₂ N) ₃ P	0.54
(Et ₂ N) ₃ P	0.27
Bu ₃ P	0.17
Mor ₃ P	0.09 ^b
(Pr ₂ N) ₃ P	0.048
(EtO) ₃ P	~ 0.003
PhPMor ₂	~ 0.0025
(MeO) ₃ P	~ 0.001
(BuO) ₃ P	~ 0.001
Ph ₃ P	0

^a K-values between 10² and 10⁻² are good to ± 10 %.

^b Determined also from the reaction between the phosphine telluride and ionic cyanide.

less double-bond character. As a result of a comparison of atom sizes, it is probable that the tendency of the chalcogen atoms to make double-bonds to the phosphorus atom decreases in the series oxygen > sulfur > selenium > tellurium.

The tellurium basicity of trivalent phosphorus species. In Table 4 are listed the experimentally determined equilibrium constants for the reactions between a number of trivalent phosphorus compounds and the tellurocyanate ion. Although these *K*-values are relative to the cyanide ion, an ionic nucleophile, they may serve as a convenient measure of the tellurium basicity of the investigated compounds.

The lack of reaction between triphenylphosphine and the tellurocyanate ion is in agreement with a previous result;^{2,3} only in the presence of small alkali ions will a reaction take place. However, the product is not the telluride, but the addition compound between the telluride and another molecule of triphenylphosphine, (Ph₃P)₂Te. It is notable that only one phenyl group linked to the phosphorus atom exerts a profound destabilization of the telluride; compare *K*-values for Mor₃P and Mor₂PPh in Table 4. No tertiary phosphine tel-

lurides containing more than one phenyl group seem to have been reported.³⁰

Similarly, the alkoxy group destabilizes to a considerable extent the phosphine tellurides and the very weak tellurium basicity of trialkyl phosphites as observed in the present study is in agreement with synthetic results. No trialkyl tellurophosphates, $(RO)_3PTe$, appear to have been synthesized and only one phosphine telluride with two alkoxy groups, allyl diethyltellurophosphonate, has been prepared.³¹ However, several tellurophosphinates, $(RO)(R'_2N)_2PTe$ and $(RO)R'_2PTe$, have been prepared.³²

The considerable tellurium basicity of Bu_3P as observed in the present study is also in agreement with synthetic results and numerous trialkylphosphine tellurides, R_3PTe , have been prepared and characterized.^{27,30,33,34}

From the stability of tris(dialkylamino)phosphine tellurides as observed in the present study, the high tellurium basicity of tris(dialkylamino)phosphines is as expected. Likewise, other trivalent phosphorus species containing an amino group in the α -position to the phosphorus atom^{22,35} are known to make fairly stable phosphine tellurides. It is apparent that amino groups linked to the phosphorus atoms exert a pronounced stabilizing influence upon the corresponding tellurides.

It was mentioned above that in phosphine tellurides the P—Te bond has a dipolar form, presumably due to the limited ability of the tellurium atom to make a double bond to the phosphorus atom. In extension of this argument, the P—Te bond will be strengthened and the stability of phosphine tellurides will be increased by strongly electron-donating groups linked to the phosphorus atom. Since the double bond character of the phosphorus—chalcogen bond is decreasing in the series $O > S > Se > Te$, the importance of arguments based upon $d_\pi - p_\pi$ bonding between the phosphorus atom and the chalcogen atom will decrease likewise. It is thus to be assumed that the arguments by McFarlane and Rycroft³⁶ are less valid for phosphine tellurides than for phosphine selenides. The stability of phosphine tellurides should thus in principle be dependent upon the σ -donor ability of the groups linked to the phosphorus atom and thus be comparable with the stability of the adducts between R_3P and BH_3 ³⁷ and the azido adducts in the Staudinger reaction.^{38,39}

However, an argument for the tellurium basicity of tris(dialkylamino)phosphines and also trialkyl-

phosphines being based entirely upon the electron donating ability of the groups linked to the phosphorus atom seems oversimplified. First of all, *n*- Bu_3P is quite comparable with $(Me_2N)_3P$ in tellurium basicity; still *tert*- Bu_3PTe is quantitatively detellurated by $(Me_2N)_3P$,¹⁰ even though *tert*- Bu_3P is considered as a significantly better donor than is Bu_3P .^{40,41} This may indicate that the bulk of the groups linked to the phosphorus atom play an important role. Furthermore, the observation that $(Et_2N)_3P$ and $(Pr_2N)_3P$ are poorer bases toward the tellurium atom than is $(Me_2N)_3P$ may suggest that the larger steric demands of these groups will prevent the lone pairs of the nitrogen atom to adjust to the desired orthogonal positions which appear to be of considerable importance for the structure of $(R_2N)_3P^2$ and $(R_2N)_3PX$.¹

The observation that Pip_3P is a better donor than Mor_3P is as anticipated since piperidine is a considerably better donor than morpholine. In the selenides derived from these aminophosphines, the P—Se bond in Pip_3PSe is slightly longer than in Mor_3PSe ¹ in agreement with the suggestion that better donors linked to the phosphorus atom will increase the polar nature of bonds between the phosphorus atom and the heavier chalcogens.

The exceptional basicity of $Pyrr_3P$ deserves some comment, especially since it has recently been shown that $Pyrr_3PO$ is a considerably better donor than $(Me_2N)_3PO$.⁴² None of the usual physical parameters for amines like hydrogen basicity,⁴³ vertical ionization potential, gas phase basicity, proton affinity or hydrogen affinity⁴⁴ suggest that the pyrrolidino group is distinctly different from the piperidino group and the dimethylamino group. The mesomeric potentials, 0.90 (Pyrr), 0.84 (Me_2N), 0.775 (Pip) and 0.74 (Mor)⁴⁵ indicate that the pyrrolidino group is a slightly better donor, but not to any significant extent.

Presumably, the unique donor ability of the pyrrolidino ring is due to the fact that the nitrogen atom is highly flexible and more easily adopts to a planar coordination. In a recent structure of a cobalt complex, the CNC bond angle was found to be 113.5° as compared to 104.7° in the free amine.⁴⁶ The pyrrolidino group is well-known to make strong bonds to sp^2 hybridized carbon atoms, and in some cases, *i.e.* enamino ketones, it has been shown that these bonds have restricted rotation. This ability to make "double" bonds with carbon atoms is far less pronounced for the piperidino nitrogen atom.^{47,48} Presumably, the pyrrolidino nitrogen

Table 5. λ_{\max} (>205 nm) with extinction coefficients ($\log \epsilon$) of Mor_3P in cyclohexane and of Mor_3PO , Mor_3PS , Mor_3PSe , Mor_3PTe , Pip_3PTe and Pyrr_3PTe in methanol.

	λ_{\max} (nm)	$\log \epsilon$
Mor_3P	$\sim 230^a$	$\sim 3.83^a$
Mor_3PO	< 205	
Mor_3PS	$\sim 210^a$	$\sim 3.70^a$
Mor_3PSe	$\sim 225^a$	$\sim 3.56^a$
Mor_3PTe	286	2.79
Pip_3PTe	288	2.85
Pyrr_3PTe	$\sim 281^a$	$\sim 2.90^a$

^a The peaks are actually shoulders to a peak of greater intensity and both λ_{\max} and the corresponding extinction coefficients are subject to some uncertainty.

atom acts similarly when located α to the phosphorus atom in tris(pyrrolidino)phosphine telluride. It is apparent that the ability of the nitrogen atom to donate electrons to the phosphorus atom and thus increase its sp^2 character is of considerable importance for the stability of aminophosphine tellurides and also selenides since caged aminophosphines, in which the nitrogen atoms only with difficulty can alter their hybridization, react only slowly with elemental selenium and are unreactive toward tellurium.⁴⁹ A crystal structure determination of tris(pyrrolidino)phosphine telluride is in progress in these laboratories.

UV and IR measurements. In Table 5 are listed the results from the UV measurements performed in the present study. The yellow colour of the tellurides is apparently due to a separate absorption owing to the phosphorus–tellurium bond in the UV-region at ~ 280 nm which stretches into the visible region. In phosphine selenides and phosphine sulfides derived from aminophosphines the corre-

Table 6. Stretching frequencies, ν_{PSe} and ν_{PTe} , for some tris(dialkylamino)phosphine selenides and tellurides (KBr-mulls).

	$\nu_{\text{PSe}} \text{ cm}^{-1}$	$\nu_{\text{PTe}} \text{ cm}^{-1}$
Mor_3PX	521	508
Pip_3PX	495	490
Pyrr_3PX	535	526
$(\text{Me}_2\text{N})_3\text{PX}^a$	530	519

^a Ref. 5.

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sponding P–X absorption is observed at ~ 230 nm and ~ 210 nm, respectively, *cf.* Ref. 50 and Table 5, with considerably greater extinction coefficients.⁵⁰ In conformity with the suggestion that these latter absorptions are due to $n-\pi^*$ transitions, one may propose that the absorptions at ~ 280 nm are due to $n-\pi^*$ transitions as well, but this assignment is only speculative.

In Table 6 are listed the stretching frequencies for some aminophosphine selenides and tellurides, $\nu_{\text{P=Se}}$ and $\nu_{\text{P=Te}}$, respectively. The surprising observation is the small difference between $\nu_{\text{P=Se}}$ and $\nu_{\text{P=Te}}$ amounting to only $\sim 10 \text{ cm}^{-1}$. Both the increase in mass from selenium to tellurium and the suggested increase in dipolar nature from the selenide to the telluride should actually cause an increase in the difference between $\nu_{\text{P=Se}}$ and $\nu_{\text{P=Te}}$; P–Te stretching frequencies were actually to be anticipated in the $300-350 \text{ cm}^{-1}$ range. It is apparent that some factors, hitherto unknown, are responsible for the high absorption frequencies due to the phosphorus–tellurium bond. Goubeau and co-workers⁵ have calculated bond orders for the P–X bonds in $(\text{Me}_2\text{N})_3\text{PX}$ and found that the bond order of the P–Te bond is significantly higher than that of the P–Se bond which is a natural conclusion from the absorption frequencies but hardly in conformity with the chemical evidence. It is apparent that for these systems the Siebert rule⁵¹ should be applied with some caution.

The data in Table 6 indicate clearly that there is apparently no correlation between the assumed donor ability of the groups linked to the phosphorus atom and the IR absorption frequencies. Since there also appears to be a lack of correlation between bond lengths and stretching frequencies in phosphine chalcogenides,^{52,53} it is conceivable that IR frequencies in this class of compounds are of limited diagnostic value when considering bond strengths.

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