

Structural Studies on the Phosphorus-Nitrogen Bond. X. The Crystal Structure of *N*-(Tris(morpholino)phosphor- anylidene)benzamide

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The structure of the title compound, $(\text{O}(\text{CH}_2\text{CH}_2)_2\text{N})_3\text{P}=\text{NC}(\text{O})\text{C}_6\text{H}_5$, has been determined from X-ray diffraction data. Full-matrix least-squares refinement led to a conventional *R*-value of 0.040 for 4033 reflections. The compound is monoclinic with the following unit cell dimensions (at -130°C): $a=8.255(1)$, $b=15.724(2)$, $c=15.444(2)$ Å; $\beta=99.68(1)^\circ$. There are four molecules in the unit cell.

The P–N bonds to the morpholino groups range from 1.642(1) to 1.663(1) Å and are slightly shorter than in the pentavalent compounds, $(\text{R}_2\text{N})_3\text{PX}$ (X=Se,Te). The sum of the bond angles to the nitrogen atoms in the morpholino groups are 348.8(3), 350.6(3) and 356.8(3)° and it is the nitrogen atom of highest sp^3 character which has its lone pair *antiperiplanar* to the P=N bond. The NPN bond angles within the N_3P part of the molecule are highly dissimilar, 102.8(1), 102.8(1) and 113.7(1)°. The sum of these bond angles is 319.3° as compared with 317.7° in Mor_3PSe .

The carbonyl group is nearly coplanar with the phenyl ring with a torsion angle of only 3.5°. The C=O bond length is 1.244(2) Å, the P=N bond length is 1.591(1) Å, the N–C(O) bond length is 1.363(2) Å and the C(O)–C bond length is 1.508(2) Å. These bond lengths have been compared with the corresponding bond lengths in $\text{Ph}_3\text{PNC}(\text{O})\text{Ph}$ and it is concluded that the P=N bond in the title compound has a higher degree of double bond character than in the compound derived from Ph_3P . The possible consequences for the stability of phosphazide adducts in the Staudinger reaction are briefly discussed.

In previous studies in this series on the structure of compounds containing the phosphorus-nitrogen bond various trivalent and pentavalent species together with phosphonium salts and phosphoranes derived from tris(dialkylamino)phosphines have been examined.¹ These compounds have been shown to be highly asymmetric with regard to the NPN bond angles, the P–N bond lengths, the hybridization of the nitrogen atoms and particularly the direction of the lone pair of the nitrogen atoms. Presently, only two compounds are known in which the dialkylamino groups are twisted in a fairly symmetrical propeller-like arrangement with all nitrogen atoms being essentially sp^2 hybridized; in the weak adduct between tris(dimethylamino)phosphine oxide and methyl-diphenylarsine sulfide² and in the 4-nitrobenzyltris(piperidino)phosphonium cation.³ These exceptions suggest that by proper choice of substituents the conformation of the compounds may

change from the apparently most stable *gauche-gauche-anti* conformation to the symmetrical propeller one.³ The various factors which are responsible for this conformational change are presently not known but the observation that the propeller-like arrangement is favoured in an adduct of a phosphine oxide² and in a phosphonium cation³ may suggest that the charge on the phosphorus atom plays an important role.

Recently, the crystal structure of a phosphorane, $\text{Mor}_3\text{P}=\text{CHC}(\text{O})\text{Ph}\cdot\text{H}_2\text{O}$ (Mor=Morpholino) was described.⁴ This compound was shown to exist in the usual asymmetrical *g-g-a* conformation. As an extension of this study we report the structure of a corresponding compound with a P=N bond, *N*-(tris(morpholino)phosphoranylidene)benzamide. This compound is readily prepared from tris(morpholino)phosphine and benzoyl azide by means of the Staudinger reaction,⁵ eqn. (1).



In a recent kinetic study of this reaction it was shown that the intermediate, the phosphazide adduct, was fairly stable for reactions of tris(dialkylamino)phosphines but appeared quite unstable for reactions of triphenylphosphine.⁵ A comparison between the structure of the title compound and that of the corresponding compound derived from Ph_3P might possibly shed some light upon the mechanism of the Staudinger reaction. The crystal structure of *N*-(triphenylphosphoranylidene)benzamide, $\text{Ph}_3\text{P}=\text{NC}(\text{O})\text{Ph}$, has recently been published.⁶

EXPERIMENTAL

Materials. Benzoyl azide, $\text{PhC}(\text{O})\text{N}_3$, was prepared as described in Ref. 7 and was purified by sublimation, m.p. 32 °C. Tris(morpholino)phosphine, Mor_3P , was prepared and purified according to a published procedure.⁸

N-(Tris(morpholino)phosphoranylidene)benzamide. To 2.9 g (0.01 mol) Mor_3P dissolved in 75 ml argon-flushed benzene was added with magnetic stirring 1.5 g (0.01 mol) benzoyl azide in 50 ml benzene through a dropping funnel. The reaction mixture turned immediately yellow and when approximately half of the azide had been added a yellow product started to precipitate. Since the decomposition of the phosphazide adduct was fairly slow at room temperature⁵ the reaction mixture was kept at ~50 °C to complete the final step of the reaction. After 3–4 h the nitrogen evolution had ceased and a colourless reaction mixture was obtained. The solvent was removed in vacuum and the residue was crystallized from a minimum amount of benzene from which suitable crystals for the X-ray study were obtained. Yield 3.9 g, 95 %, m.p. 165 °C.

X-Ray data. Data were collected on a SYNTEX $P\bar{1}$ diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.71069$ Å). The temperature at the crystal site was ~–130 °C. The crystal size was approximately 0.2×0.1×0.3 mm. Cell parameters were determined by a least-squares fit to the diffractometer setting of 15 general reflections with $2\theta>30^\circ$. The intensities were collected with the $\theta-2\theta$ technique; scan speed 4° min⁻¹, scan width –0.9 to +1.1 up to a $\sin \theta/\lambda$ value of 0.70 Å⁻¹. Background counts were taken at each of the scan limits for 0.35 times the scan time. Out of 5343 unique reflections measured 4033 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 intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu=1.0$ cm⁻¹).

A description of the computer program applied for the structure analysis is given in Ref. 9. Atomic scattering factors were those of Doyle and Turner¹⁰ for the heavy atoms and of Stewart, Davidson and Simpson¹¹ for the hydrogen atoms.

Table 1. Fractional atomic coordinates with estimated standard deviations for *N*-(tris(morpholino)phosphoranylidene)benzamide.

Atom	X	Y	Z	H-atoms	X	Y	Z
P	.6342(1)	.2277(0)	.2930(0)	H3	.6408	.1108	.5198
N1	.7978(2)	.2660(1)	.2570(1)	H4	.6707	.0289	.6479
N2	.5625(2)	.3125(1)	.3376(1)	H5	.7971	-.1054	.6501
N3	.5168(2)	.1943(1)	.2025(1)	H6	.9014	-.1519	.5254
N4	.6568(2)	.1588(1)	.3694(1)	H7	.8647	-.0672	.3951
O4	.7722(2)	.0510(1)	.2975(1)	H111	1.0006	.2768	.3538
C1	.7267(2)	.0815(1)	.3636(1)	H112	.8668	.3505	.3550
C2	.7461(2)	.0298(1)	.4469(1)	H121	1.1069	.4021	.3044
C3	.6900(2)	.0582(1)	.5217(1)	H122	.9398	.4118	.2254
C4	.7095(2)	.0087(1)	.5970(1)	H131	1.0431	.2366	.1115
C5	.7849(2)	-.0699(1)	.5965(1)	H132	.9025	.3089	.1101
C6	.8427(3)	-.0985(1)	.5244(1)	H141	.7989	.1830	.1563
C7	.8235(2)	-.0491(1)	.4493(1)	H142	.9589	.1705	.2327
C11	.9213(2)	.3152(1)	.3174(1)	H211	.4304	.3939	.2476
C12	1.0171(2)	.3702(1)	.2638(1)	H212	.6247	.4046	.2538
O1	1.0982(1)	.3190(1)	.2071(1)	H221	.5054	.5178	.3238
C13	.9793(2)	.2714(1)	.1481(1)	H222	.6415	.4634	.3955
C14	.3805(2)	.2140(1)	.1976(1)	H231	.3452	.3691	.4871
C21	.5357(2)	.3942(1)	.2897(1)	H232	.5398	.3800	.4952
C22	.5318(2)	.4658(1)	.3544(1)	H241	.4617	.2497	.4272
O2	.4035(2)	.4526(1)	.4048(1)	H242	.3244	.2912	.3605
C23	.4340(2)	.3754(1)	.4538(1)	H311	.3465	.2753	.1376
C24	.4371(2)	.2993(1)	.3940(1)	H312	.5259	.3048	.1322
C31	.4529(2)	.2533(1)	.1308(1)	H321	.5526	.1979	.0310
C32	.4401(2)	.2098(1)	.0427(1)	H322	.3834	.2472	-.0020
O3	.3436(2)	.1327(1)	.0388(1)	H331	.5322	.0604	.0989
C33	.4195(3)	.0758(1)	.1071(1)	H332	.3514	.0250	.0988
C34	.4212(2)	.1152(1)	.1963(1)	H341	.4655	.0770	.2399
				H342	.3117	.1253	.2030

CRYSTAL DATA

N-(Tris(morpholino)phosphoranylidene)benzamide, C₁₉H₂₉N₄O₄P, m.p. 165 °C. Monoclinic, $a=8.255(1)$ Å; $b=15.724(2)$ Å; $c=15.444(2)$ Å; $\beta=99.68(1)^\circ$; $V=1976.2(5)$ Å³ ($t=-130$ °C); $M=408.44$; $Z=4$; $F(000)=832$; $D_x=1.2096$ gcm⁻³. Absent reflections: ($h0l$) for $h+l$ odd, ($0k0$) for k odd. Space group $P2_1/n$ (No. 14).

STRUCTURE DETERMINATION

The structure was determined by direct methods and refined using anisotropic temperature factors for nonhydrogen atoms as described in Ref. 8. The refinement converged to a conventional R -value of 0.040, $R_w=0.039$, and a goodness of fit equal to $[\sum w\Delta F^2/(m-n)]^{1/2}$ of 1.65.

Final atomic parameters are listed in Table 1. Tables containing observed and calculated structure factors and anisotropic temperature factors are available from the authors.

ORTEP drawing of the molecule is shown in Fig. 1 where the numbering of the atoms is also indicated. Bond lengths, bond angles, torsion angles and various other structural and derived data are listed in Table 2. The estimated standard deviations are calculated from the variance-covariance matrix.

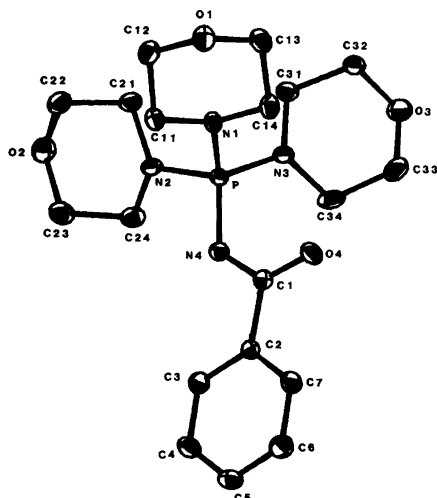


Fig. 1. ORTEP drawing of *N*-(tris(morpholino)phosphoranylidene)benzamide.

RESULTS AND DISCUSSION

General remarks. In Table 3 are collected some important structural parameters in *N*-(tris(morpholino)phosphoranylidene)benzamide from the present study, in the phosphorane derived from tris(morpholino)phosphine and phenacyl bromide, $\text{Mor}_3\text{P}=\text{CH}-\text{C}(\text{O})\text{Ph}\cdot\text{H}_2\text{O}$, from Ref. 4 and in tris(morpholino)phosphine selenide, Mor_3PSe , from Ref. 12. The latter two compounds were chosen for comparison since the phosphorus–nitrogen bond lengths in these two compounds are fairly similar to the ones observed in $\text{Mor}_3\text{P}=\text{NC}(\text{O})\text{Ph}$, the title compound. The structural parameters as listed in Table 3 show clearly that the three compounds are structurally quite similar with regard to the PN_3 part of the molecules. Fig. 2 shows Newman projections along the four P–N bonds in the title compound. The asymmetric *g-g-a* conformation is observed for all three

Table 2. Structural data.

Bond lengths (Å)					
P	N1	1.650(1)	O1	C13	1.424(2)
P	N2	1.663(1)	C13	C14	1.500(2)
P	N3	1.642(1)	C14	N1	1.485(2)
P	N4	1.591(1)	N2	C21	1.484(2)
N4	C1	1.363(2)	C21	C22	1.510(2)
C1	O4	1.244(2)	C22	O2	1.429(2)
C1	C2	1.508(2)	O2	C23	1.434(2)
C2	C3	1.391(2)	C23	C24	1.516(2)
C2	C7	1.403(2)	C24	N2	1.474(2)
C3	C4	1.388(2)	N3	C31	1.478(2)
C4	C5	1.391(3)	C31	C32	1.510(2)
C5	C6	1.388(2)	C32	O3	1.415(2)
C6	C7	1.384(2)	O3	C33	1.437(2)
N1	C11	1.470(2)	C33	C34	1.508(3)
C11	C12	1.502(2)	C34	N3	1.457(2)
C12	O1	1.441(2)			

Table 2. Continued.

Bond angles (°)				
N1	P	N2	102.8(1)	
N1	P	N3	102.8(1)	
N1	P	N4	119.2(1)	
N2	P	N3	113.7(1)	
N2	P	N4	104.5(1)	
N3	P	N4	113.5(1)	
P	N4	C1	124.3(1)	
N4	C1	C4	126.4(2)	
O4	C1	C2	119.1(1)	
N4	C1	C2	114.5(1)	
C1	C2	C3	122.0(1)	
C1	C2	C7	119.1(1)	
C2	C3	C4	120.3(2)	
C3	C4	C5	120.5(2)	
C4	C5	C6	119.7(2)	
C5	C6	C7	119.9(2)	
C6	C7	C2	120.7(2)	
C7	C2	C31	118.9(1)	
P	N1	C11	119.2(1)	
P	N1	C14	119.9(1)	
C11	N1	C14	109.7(1)	
N1	C11	C12	108.4(1)	
C11	C12	O1	110.8(1)	
C12	O1	C13	109.9(1)	
O1	C13	C14	110.8(1)	
C13	C14	N1	109.2(1)	
P	N2	C21	122.0(1)	
P	N2	C24	118.3(1)	
C21	N2	C24	110.3(1)	
N2	C21	C22	109.6(1)	
C21	C22	O2	111.2(1)	
C22	O2	C23	108.6(1)	
O2	C23	C24	111.6(1)	
C23	C24	N2	110.1(1)	
P	N3	C31	121.8(1)	
P	N3	C34	123.6(1)	
C31	N3	C34	111.4(1)	
N3	C31	C32	110.5(1)	
C31	C32	O3	112.2(1)	
C32	O3	C33	110.7(1)	
O3	C33	C34	110.6(2)	
C33	C34	N3	109.2(1)	
Torsion angles (°)				
N2	P	N1	C11	51.5(1)
N2	P	N1	C14	-168.4(1)
N3	P	N1	C11	169.9(1)
N3	P	N1	C14	-50.0(1)
N4	P	N1	C11	-63.5(1)
N4	P	N1	C14	76.5(1)
N1	P	N2	C21	50.1(1)
N1	P	N2	C24	-166.7(1)
N3	P	N2	C21	-60.2(1)
N3	P	N2	C24	82.9(1)
N4	P	N2	C21	175.5(1)
N4	P	N2	C24	-41.4(1)
N1	P	N3	C31	-62.5(1)
N1	P	N3	C34	139.6(1)
N2	P	N3	C31	48.0(1)
N2	P	N3	C34	-110.0(1)
N4	P	N3	C31	167.3(1)
N4	P	N3	C34	9.3(1)
N1	P	N4	C1	-60.0(1)
N2	P	N4	C1	-174.1(1)
N3	P	N4	C1	61.4(1)
Various averaged and derived data				
N _x	N1	N2	N3	
$\overline{\text{N}-\text{C}}$ (Å)	1.478	1.479	1.468	
$\overline{\text{C}-\text{C}}$ (Å)	1.501	1.513	1.509	
$\overline{\text{O}-\text{C}}$ (Å)	1.433	1.432	1.426	
$\overline{\text{C}-\text{C}}$ (Aryl) (Å)		1.391		

compounds. In previous studies in this series the longest P–N bond was generally observed for the bond to the one nitrogen atom of highest *p*-character which was also the atom with its lone pair being *antiperiplaner* to the phosphorus lone pair or to the P=X bond. In the phosphorane, however, only the first part of this pattern is obeyed, *cf.* Table 3. In the compound studied in the present study the longest P–N bond is undoubtedly the one to N2

Table 3. A comparison between some structural parameters in $\text{Mor}_3\text{P}=\text{NC}(\text{O})\text{Ph}^a$, in $\text{Mor}_3\text{P}=\text{NC}(\text{O})\text{Ph}$, in $\text{Mor}_3\text{P}=\text{CHC}(\text{O})\text{Ph} \cdot \text{H}_2\text{O}$ and in $\text{Mor}_3\text{P}=\text{Se}$.

	$\text{Mor}_3\text{P}=\text{NC}(\text{O})\text{Ph}^a$			$\text{Mor}_3\text{P}=\text{CHC}(\text{O})\text{Ph} \cdot \text{H}_2\text{O}^b$			$\text{Mor}_3\text{P}=\text{Se}^c$		
	N1^d	N2	N3^e	N1	N2^d	N3^e	N1^d	N2	N3^e
$\Sigma \angle \text{N}$ ($^\circ$)	348.8(3)	350.6(3)	356.8(3)	348.7(4)	355.8(4)	359.6(4)	340.1(2)	349.7(2)	354.9(2)
Tors. angle ($^\circ$)	-173.5	67.1	-91.7	-57.1	168.8	81.8	-178.9	65.8	-77.6
P-N (Å)	1.650(1)	1.663(1)	1.642(1)	1.668(2)	1.645(2)	1.641(2)	1.684(2)	1.670(2)	1.661(2)
$\angle \text{NPN}$ ($^\circ$)	113.7(1)	102.8(1)	102.8(1)	104.1(1)	113.8(1)	103.1(1)	114.1(1)	102.4(1)	101.2(1)
$\Sigma \text{P-N}$ (Å)		4.955(3)			4.954(6)			5.015(6)	
ΣNPN ($^\circ$)		319.3(3)			321.0(3)			317.7(6)	
$\angle \text{NP=X}$ ($^\circ$)	119.2(1)	104.5(1)	113.5(1)	106.0(1)	117.9(1)	112.0(1)	115.1(1)	112.0(1)	112.0(1)
P=X (Å)		1.591(1)			1.717(2)			2.106(1)	

^a This study. ^b From Ref. 4. ^c From Ref. 12. ^d The nitrogen atom with its lone pair *antiperiplanar* to the P=X bond (X=N, C and Se). ^e The nitrogen atom with lone pair of lowest *p*-character. ^f Bond angle to nitrogen atoms other than N_x .

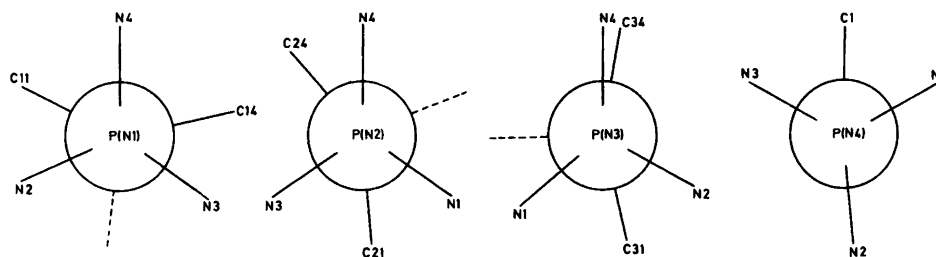


Fig. 2. Newman projections along the four phosphorus–nitrogen bonds, P–N1, P–N2, P–N3 and P=N4.

which is not the nitrogen atom of highest *p*-character. The nitrogen atom of highest *p*-character, N1, has its lone pair *antiperiplanar* to the P=N bond. The difference in the hybridization of the two nitrogen atoms, N1 and N2, however, is small as viewed by the sum of the bond angles to these atoms, *cf.* first entry in Table 3. As in the phosphorane and in the selenide the shortest P–N bond is to the nitrogen atom of highest *s*-character. In none of the compounds studied so far has the atom of highest *s*-character been observed to have its lone pair *antiperiplanar* to the phosphorus lone pair in the trivalent compounds or to the P=X bond in the pentavalent compounds.

The sum of the NPN bond angles is close to 320° and is as observed in the phosphorane and in the selenide, *cf.* Table 3. The NP=N bond angles are seen to be highly different, $119.2(1)$, $104.5(1)$ and $113.5(1)^\circ$; the larger bond angle to the nitrogen atom being *antiperiplanar* to the P=N bond. This observation is in agreement with the results from previous studies.¹² Since the asymmetry with regard to the NP=X bond angles seems to decrease with increasing P=X bond length; *cf.* last entry in Table 3, one may conclude that this asymmetry is of steric origin.

The P=NC(O)Ph part of the molecule. The P=N bond is only $1.591(1)\text{Å}$ and a bond length of this order of magnitude suggests that this bond has a considerable double bond character; *cf.* Ref. 13 for a survey of phosphorus–nitrogen bond lengths. Although the P=N bond is short and the N=C bond is as expected for a N–C_{sp²} bond, the P=N bond cannot be a pure double bond. The C=O bond length of $1.244(2)\text{Å}$, significantly longer than a bond between carbon and oxygen in carbonyl compounds, $1.215\text{--}1.225\text{Å}$,⁴ indicates some conjugation within the P=N–C=O part of the molecule. The C=O bond length, however, is slightly but significantly shorter than was observed in the phosphorane derived from Mor_3P , $\text{Mor}_3\text{P}=\text{CHC}(\text{O})\text{Ph}\cdot\text{H}_2\text{O}$, $1.258(3)\text{Å}$.⁴ This suggests that the dipolar nature of the P=N bond in the title compound is less pronounced than in the phosphorane with a P=C bond. The bond between the carbonyl group and the phenyl ring is $1.508(2)\text{Å}$ and does not indicate that the phenyl group takes part in any conjugation. Further evidence for this suggestion can be found in the various bond angles and bond lengths in the phenyl group which are all as expected for a non-conjugated group, *cf.* Table 2.

The carbonyl group is nearly coplanar with the phenyl group with a torsion angle of only 3.5° . The sum of the bond angles to the carbonyl carbon atom is $360.0(2)^\circ$. The NCO bond angle is significantly larger than the NCC bond angle, $126.4(2)$ and $114.5(2)^\circ$, respectively. A similar asymmetry with regard to the bond angles to the carbonyl carbon atom was observed in $\text{Ph}_3\text{P}=\text{NC}(\text{O})\text{Ph}$.⁶ This increase in the NCO bond angle may be due to the groups linked to the phosphorus atom and thus be of steric origin.

The morpholino substituents. The morpholino substituents are all in the expected chair conformation and are linked to the phosphorus atom in an approximately equatorial direction. All bond angles and bond lengths as listed in Table 2 are as expected.

Comments on the mechanism of the Staudinger reaction. From a kinetic study on the Staudinger reaction, eqn. (1), it was recently suggested that the following steps might take place, particularly for reactions of tris(dialkylamino)phosphines:⁵ (i) Nucleophilic attack at the nitrogen atom adjacent to the carbonyl group forming the branched phosphazide adduct, $(R_2N)_3PN(N_2)C(O)R$; (ii) a rapid sigmatropic shift to the linear phosphazide adduct, $(R_2N)_3PN_3C(O)R$; (iii) a final intramolecular or intermolecular attack by the nitrogen atom adjacent to the carbonyl group at the phosphorus atom forming the substituted benzamide and molecular nitrogen.

Leffler and co-workers¹⁴ have previously shown that when triphenylphosphine, Ph_3P , reacts with aroyl azides the first step is the rate determining one. In the case of tris(dialkylamino)phosphines, $(R_2N)_3P$, however, the first step is rapid while the final step is slow.⁵ While the low rate of the first step for the reactions of Ph_3P with the aroyl azides can be accounted for by the fairly low nucleophilicity of this compound toward tervalent nitrogen, the question arises why the linear phosphazide adduct is considerably more stable when derived from $(R_2N)_3P$ than from Ph_3P .

In Table 4 a comparison is made between some important structural parameters in $Mor_3P=NC(O)Ph$ as obtained in the present study and in $Ph_3P=NC(O)Ph$ from Ref. 6. From the P–N bond lengths it is clear that the double bond character of the phosphorus-nitrogen bond in the compound derived from the aminophosphine is significantly greater than in $Ph_3P=NC(O)Ph$. Since the dipolar nature of the P=N bond in the compound derived from Ph_3P seems to exceed that of the P=N bond in the benzamide derived from Mor_3P , the electrophilic nature of the phosphorus atom in the phosphazide adduct from Ph_3P will presumably also exceed that of the phosphorus atom in the corresponding adduct from Mor_3P . The higher rate for the last step in the Staudinger reaction with Ph_3P can thus be accounted for.

It is notable that the pronounced difference in the P=N bond lengths in the two compounds is not accompanied by significant differences in the adjacent bonds; *cf.* Table 4. The sum of the NPN and the CPC bond angles, however, are significantly different, 319.3 and 322.6°, respectively. This difference accords with the suggestion that the phosphonium character of the substituted benzamide derived from Ph_3P exceeds that of the corresponding

Table 4. A comparison between some structural parameters in $Mor_3P=NC(O)Ph$ and in $Ph_3P=NC(O)Ph$.

	$Mor_3P=NC(O)Ph^a$	$Ph_3P=NC(O)Ph^b$
P=N (Å)	1.591(1)	1.626(3)
N–C (Å)	1.363(2)	1.353(5)
C=O (Å)	1.244(2)	1.245(5)
C–C (Å)	1.508(2)	1.504(4)
$\angle P=NC$ (°)	124.3(1)	117.8(3)
$\Sigma \angle NPN, \Sigma \angle CPC$ (°)	319.3(3)	322.6(6)
$\Sigma \angle NP=N, \Sigma \angle CP=N$ (°)	337.2(3)	333.3(6)
$\Sigma \angle C(O)$ (°)	360.0(2)	360.0(2)

^a This study. ^b From Ref. 6.

compound made from Mor_3P . The different P=NC bond angles, 124.3 and 117.8°, may be due to the difference in the bond order of the P=N bonds in the two compounds.

Recently,⁴ a similar comparison between some structural parameters in $\text{Mor}_3\text{P}=\text{CHC}(\text{O})\text{Ph}\cdot\text{H}_2\text{O}^4$ and in $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{Ph}^{15}$ revealed that none of the bond lengths, including the P=C bond lengths, or any of the bond angles were significantly different in the two compounds. Apparently, while tris(dialkylamino)phosphines are superior to triphenylphosphine to make a double bond to a nitrogen atom, these trivalent phosphorus species are linked fairly similarly to the carbon atom in phosphoranes. While phosphoranes derived from $(\text{R}_2\text{N})_3\text{P}$ and from Ph_3P may behave chemically quite similarly, e.g. toward carbonyl compounds in the Wittig reaction, the corresponding benzamides, $(\text{R}_2\text{N})_3\text{P}=\text{NC}(\text{O})\text{R}'$ and $\text{Ph}_3\text{P}=\text{NC}(\text{O})\text{R}'$, may exhibit significant differences in their reactivity.

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