

Structural Studies on the Phosphorus-Nitrogen Bond. IX. The Crystal Structures of Phenacyl Tris(morpholino)- phosphonium Bromide Monohydrate and Phenacylidene Tris(morpholino)phosphorane Monohydrate

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The structures of the title compounds, $[(O(CH_2CH_2)_2N)_3PCH_2C(O)C_6H_5]^+Br^- \cdot H_2O$, I, and $(O(CH_2CH_2)_2N)_3PCHC(O)C_6H_5 \cdot H_2O$, II, have been determined from X-ray diffraction data. Full-matrix least-squares refinement led to a conventional *R*-value of 0.065 for 3110 reflections for I and 0.040 for 2885 reflections for II.

The crystals are monoclinic, space group $P2_1/n$, with cell dimensions (at $-130^\circ C$): $a=10.883(3)$, $b=16.685(5)$, $c=12.557(3)$ Å; $\beta=91.18(2)^\circ$ for compound I and $a=16.419(5)$, $b=8.659(2)$, $c=16.411(4)$ Å; $\beta=115.16(2)^\circ$ for compound II.

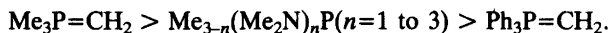
In both compounds the lone pair of one of the nitrogen atoms is *antiperiplanar* to the phosphorus-carbon bond; the lone pairs of the two other nitrogen atoms are in both compounds approximately orthogonal to this bond and are twisted in opposite direction. In I the nitrogen atoms are essentially sp^2 hybridized while in II the sum of the bond angles to one of the nitrogen atoms is only 348.7° . The one morpholino group containing this nitrogen atom is linked axially to the central phosphorus atom. Both compounds are highly asymmetric with regard to the NPN bond angles, the sum of these is 327.8° in I and 321.0° in II. The P–N bond lengths vary from 1.608(5) to 1.644(5) Å in I and from 1.632(2) to 1.668(2) Å in II.

The bond lengths in the P–C–C(O) part of I are as expected; P–C=1.791(6) Å, C–C=1.516(8) Å and C=O=1.217(7) Å. The corresponding bond lengths in II are 1.717(2), 1.399(3) and 1.258(3) Å and suggest a high degree of conjugation.

The ^{13}C -NMR spectra of I and II are presented and are compared with the spectra of the corresponding compounds derived from Ph_3P and Ph_3As . The spectra suggest that the conjugation in II is slightly less pronounced than in the corresponding phosphorane derived from Ph_3P .

Phosphoranes derived from tris(dialkylamino)phosphines, $(R_2N)_3P=CR_2$, are a group of compounds which may be considered as ylides and hence as valuable reagents in the Wittig reaction. These compounds, however, have not been the subject of detailed studies, as have corresponding compounds derived from other trivalent phosphorus compounds, particularly triphenylphosphine. Issleib and co-workers^{1,2} prepared several phosphoranes with

dialkylamino groups linked to the phosphorus atom and from their apparent stability suggested the following reactivity order:

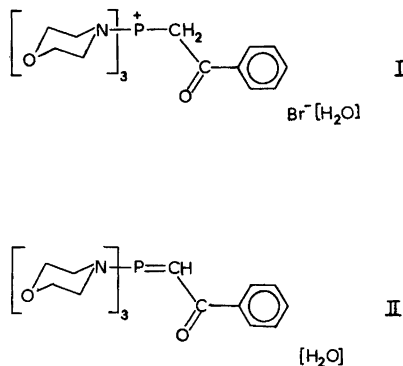


No kinetic or basicity studies have as yet been performed which might serve as a confirmation of the suggested reactivity order.

Since the reactivity of phosphoranes seems to be closely related to their ylidic nature, the question arises in which way and to what extent amino groups linked to the central phosphorus atom are influencing the phosphorus-carbon bond in this class of compounds as compared to the usual alkyl and phenyl substituents. X-ray crystallographic studies on phosphoranes derived from tris(dialkylamino)phosphines therefore appear to be a useful approach, particularly since structural data on aminosubstituted phosphoranes are presently limited.³

The crystal structures of the 4-nitrobenzylphosphonium salts derived from tris(morpholino)phosphine and from tris(piperidino)phosphine were recently described.⁴ The phosphoranes derived from these two phosphonium salts are not readily attacked by crystallographic methods since suitable crystalline samples are most difficult to prepare owing to their instability. Phosphoranes derived from phenacylphosphonium salts, $\text{PhC}(\text{O})\text{CH}_2\text{P}^+\text{R}_3 \text{X}^-$, are generally known to be stable and nicely crystalline compounds and we have chosen to investigate them. In the present study we report on the synthesis and the structure of phenacyl tris(morpholino)phosphonium bromide monohydrate, I, and the corresponding phosphorane, phenacylidene tris(morpholino)phosphorane monohydrate, II, with molecular formulae as shown in Scheme 1. Since all attempts to obtain suitable crystals of the compounds without crystal water failed, the monohydrates had to be used for the structural study. The crystal structures of the corresponding phosphonium salt and the phosphorane derived from triphenylphosphine, Ph_3P , and also the corresponding arsorane derived from triphenylarsine, Ph_3As , have recently been published⁵ and allow a comparison to be made.

The crystal structures of the parent phosphine, Mor_3P ,⁶ and of several pentavalent derivatives, Mor_3PX ($\text{X}=\text{O}, \text{Se}$ and Te),⁷ have also been determined. It was of interest to examine whether the P-C bond in I and the P=C bond in II would function conformationally similarly to the phosphorus lone pair in Mor_3P and the P=X bond in Mor_3PX with regard to the direction of the lone pair of the nitrogen atoms.



Scheme 1.

EXPERIMENTAL

Materials. Acetonitrile. *Baker Analyzed Reagent*, was distilled from phosphorus pentoxide and then from calcium hydride. The purified solvent was stored over Linde 4 Å molecular sieves in darkness. The hydrocarbons and diethyl ether were treated with metallic sodium prior to use. Tris(morpholino)phosphine was prepared from phosphorus trichloride and morpholine as previously described.⁶ The product was repeatedly crystallized from benzene to remove traces of morpholinium hydrochloride. 2-Bromo-1-phenylethanone, phenacyl bromide, a commercial product, was crystallized from acetonitrile, diethyl ether and finally from light petroleum ether (40–60 °C) prior to use.

Phenacyl tris(morpholino)phosphonium bromide monohydrate, I. To a stirred solution of 2.89 g (0.01 mol) tris(morpholino)phosphine in 150 ml acetonitrile in an argon atmosphere was added a solution of 1.99 g (0.01 mol) phenacyl bromide in 20 ml acetonitrile. The reaction mixture was left at room temperature overnight to complete the reaction. 150 ml diethyl ether was then added and the solution was kept at 0 °C for crystallization. After 24 h a white crystalline product had precipitated which was washed with diethyl ether and dried in vacuum; yield 0.9 g. The solubility of this compound in acetonitrile was limited but sufficient to allow a crystallization from this solvent. The colourless crystals, m.p. 223 °C, were suitable for an X-ray study. The X-ray analysis revealed that this compound was not the desired product but phenacyl morpholinium bromide, $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{CH}_2\text{NH}(\text{CH}_2\text{CH}_2)_2\text{O}]^+\text{Br}^-$. Whether this salt was a by-product from the reaction or a decomposition product was not further examined.

The filtrate from the reaction mixture was evaporated to dryness and the residue was washed with benzene to remove unreacted starting materials and non-ionic compounds. After several crystallizations from acetonitrile/diethyl ether a yield of 2.9 g, 59 %, of phenacyl tris(morpholino)phosphonium bromide monohydrate was obtained with crystals of satisfactory quality for the X-ray study. (Found: C 49.53; H 6.49; N 8.29; P 6.34; Calc. for $\text{C}_{20}\text{H}_{33}\text{N}_3\text{O}_5\text{PBr}$: C 48.98; H 6.78; N 8.57; P 6.32). M.p. 176–178 °C. IR(KBr-pellet): 3485(s), 3370(s), 3425(m) cm^{-1} , O–H str. and 1673 cm^{-1} , C=O str. $^1\text{H NMR}(\text{CD}_3\text{CN})$: δ 7.55–8.21 (*m*, Ph); 5.05 (*d*, CH_2 ; $J_{\text{P-H}}=14.3$ Hz); 3.63 (*m*, O– CH_2); 3.26 (*m*, N– CH_2); 2.29 (*s*, H_2O).

Phenacylidene tris(morpholino)phosphorane monohydrate, II; To a stirred solution of 2 g of I in 30 ml water was added a solution of 0.5 g NaHCO_3 in 20 ml water. After one h the product had precipitated and was dried in vacuum. Two crystallizations from benzene gave a pure product with crystals suitable for the X-ray study, m.p. 146 °C. IR(KBr-pellet): 3520(s), 3400(s), 3340(m), 3260(w), O–H str. and 1520 cm^{-1} , C=O str.

Spectroscopic measurements. A Perkin Elmer 399B Infrared Spectrophotometer was used for the IR measurements. The $^{13}\text{C NMR}$ and the $^1\text{H NMR}$ spectra were obtained at 22.63 MHz and at 90 MHz, respectively, at ambient probe temperature (*ca.* 30 °C) with a BRUKER CXP 100 spectrometer. The concentration of the solutions was approximately 0.01 M. Acetonitrile- d_6 was used as solvent and as internal ^2H -lock signal source.

X-ray data. Data for the measurements of cell dimensions and of intensity data were collected on a Nicolet P3/F 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 $\sim 0.1 \times 0.2 \times 0.3$ mm for I and $\sim 0.2 \times 0.2 \times 0.3$ mm for II. Cell parameters for the two compounds were determined by a least-squares fit to the diffractometer setting of 24 general reflections with $2\theta > 30^\circ$. Intensities were measured with the θ - 2θ scan technique. The scan speed was $2\text{--}4^\circ \text{min}^{-1}$ for I depending upon the peak intensity with a scan width of $\pm 1.0^\circ$ up to a $\sin\theta/\lambda$ value of 0.65 \AA^{-1} . For II the scan speed was 3°min^{-1} with a scan width of $-0.9\text{--}\pm 1.0^\circ$ up to a $\sin\theta/\lambda$ value of 0.59 \AA^{-1} . Background counts were for both compounds taken as 0.35 times the scan time of each of the scan limits. Out of 5736 unique reflections recorded for I 3110 with $I > 2.5\sigma(I)$ were retained for the structural analysis; the corresponding numbers for II were 4183 and 2885. The standard deviations for the intensities were calculated as $\sigma(I)=[C_T+(00.02)C_N^2]^{1/2}$, 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 effects but not for absorption.

A description of the computer programs applied for the structure determinations is given in Ref. 8. Atomic form factors were those of Doyle and Turner⁹ for the heavy atoms and of Stewart, Davidson and Simpson¹⁰ for the hydrogen atoms.

CRYSTAL DATA

I. Phenacyl tris(morpholino)phosphonium bromide monohydrate, $[(O(CH_2CH_2)_2N)-PCH_2C(O)C_6H_5]^+ Br^- \cdot H_2O$. M.p. 176–178 °C. Monoclinic, $a=10.883(3)$ Å; $b=16.685(5)$ Å; $c=12.557(3)$ Å; $\beta=91.18(2)^\circ$; $V=2279.6$ Å³ ($t=-130$ °C); $M=490.38$; $Z=4$; $F(000)=1056$; $D_x=1.428$ g cm⁻³. Absent reflections: ($h0l$) for $h+l$ odd, ($0k0$) for k odd. Space group $P2_1/n$ (No. 14).

Table I. Fractional atomic coordinates with estimated standard deviations for phenacyl tris(morpholino)phosphonium bromide monohydrate, I, and phenacylidene tris(morpholino)phosphorane monohydrate, II.

I				II			
Atom	X	Y	Z	Atom	X	Y	Z
OW	0.2196(5)	0.0491(3)	1.0077(4)	P	0.7800(0)	0.3322(1)	0.0500(0)
Br	0.5624(1)	0.2783(0)	0.4415(1)	O4	0.6843(1)	0.0618(2)	-0.0646(1)
P	0.7224(1)	0.1778(1)	0.0845(1)	C1	0.8107(1)	0.2222(3)	-0.0194(1)
O4	0.5994(4)	0.1800(3)	-0.1309(3)	C2	0.7599(1)	0.0926(3)	-0.0627(1)
C1	0.7809(5)	0.1370(4)	-0.0362(4)	C3	0.7961(1)	-0.0186(3)	-0.1104(1)
C2	0.6994(5)	0.1475(4)	-0.1345(4)	C4	0.7360(2)	-0.1228(3)	-0.1714(2)
C3	0.7454(5)	0.1129(4)	-0.2354(4)	C5	0.7654(2)	-0.2297(3)	-0.2156(2)
C4	0.8581(6)	0.0727(4)	-0.2411(5)	C6	0.8549(2)	-0.2364(3)	-0.1994(2)
C5	0.8944(6)	0.0405(4)	-0.3390(5)	C7	0.9152(2)	-0.1334(3)	-0.1398(2)
C6	0.8206(6)	0.0482(4)	-0.4277(5)	C8	0.8858(2)	-0.0248(3)	-0.0957(2)
C7	0.7103(6)	0.0888(4)	-0.4226(5)	N1	0.8601(1)	0.4655(2)	0.0946(1)
C8	0.6732(5)	0.1215(4)	-0.3280(5)	C11	0.8836(2)	0.5614(3)	0.0335(2)
N1	0.5816(4)	0.1514(3)	0.1141(4)	C12	0.9772(2)	0.6252(3)	0.0843(2)
C11	0.5510(5)	0.0693(4)	0.1484(5)	O1	0.9846(1)	0.7148(2)	0.1600(1)
C12	0.4561(6)	0.0749(4)	0.2344(5)	C13	0.9609(2)	0.6228(3)	0.2189(2)
O1	0.3482(4)	0.1157(3)	0.1960(4)	C14	0.8683(2)	0.5609(3)	0.1715(2)
C13	0.3776(6)	0.1961(4)	0.1643(5)	N2	0.7778(1)	0.2483(2)	0.1390(1)
C14	0.4705(5)	0.1948(4)	0.0762(5)	C21	0.8605(1)	0.1926(3)	0.2137(1)
N2	0.8068(4)	0.1368(3)	0.1784(4)	C22	0.8658(2)	0.0180(3)	0.2154(2)
C21	0.9325(5)	0.1052(4)	0.1655(4)	O2	0.7879(1)	-0.0494(2)	0.2183(1)
C22	1.0235(6)	0.1478(4)	0.2381(5)	C23	0.7099(2)	-0.0043(3)	0.1405(2)
O2	0.9879(4)	0.1429(3)	0.3482(3)	C24	0.6971(1)	0.1686(3)	0.1365(1)
C23	0.8704(6)	0.1807(4)	0.3576(5)	N3	0.6785(1)	0.4044(2)	-0.0036(1)
C24	0.7741(5)	0.1382(4)	0.2925(4)	C31	0.6269(2)	0.4036(3)	-0.1015(2)
N3	0.7226(4)	0.2740(3)	0.0766(3)	C32	0.6060(2)	0.5672(3)	-0.1351(2)
C31	0.6779(6)	0.3249(4)	0.1662(5)	O3	0.5572(1)	0.6466(2)	-0.0928(1)
C32	0.7745(7)	0.3838(4)	0.1998(5)	C33	0.6106(2)	0.6530(3)	0.0018(2)
O3	0.8066(4)	0.4337(3)	0.1132(3)	C34	0.6333(2)	0.4934(3)	0.0418(2)
C33	0.8541(6)	0.3855(4)	0.0283(5)	OW1	0.9947(3)	0.5831(6)	0.5855(3)
C34	0.7639(6)	0.3257(4)	-0.0122(5)	OW2	0.9799(3)	0.4966(5)	0.5739(3)
H11	0.801	0.071	-0.027	H1	0.866	0.243	-0.019
H12	0.847	0.146	-0.049	H4	0.675	-0.118	-0.182
H4	0.911	0.073	-0.176	H5	0.724	-0.295	-0.256
H5	0.989	0.010	-0.324	H6	0.876	-0.304	-0.229
H6	0.856	0.018	-0.486	H7	0.982	-0.136	0.126
H7	0.673	0.100	-0.480	H8	0.927	0.046	-0.057
H8	0.602	0.170	-0.327	H111	0.840	0.648	0.010
H111	0.634	0.046	0.170	H121	0.992	0.693	0.043
H112	0.504	0.032	0.084	H131	0.966	0.686	0.267
H122	0.423	0.018	0.251	H141	0.850	0.499	0.212
H132	0.291	0.215	0.124	H211	0.858	0.229	0.266
H142	0.446	0.164	0.021	H221	0.915	-0.013	0.270
H212	0.939	0.040	0.193	H231	0.658	-0.054	0.145
H222	1.091	0.117	0.233	H241	0.685	0.205	0.189
H232	0.868	0.185	0.430	H311	0.569	0.348	-0.118
H242	0.775	0.082	0.319	H321	0.570	0.573	-0.198
H312	0.596	0.342	0.134	H331	0.577	0.706	0.031
H322	0.728	0.418	0.260	H341	0.578	0.441	0.034
H332	0.875	0.432	-0.021	HW14	0.943	0.568	0.581
H342	0.680	0.343	-0.061	HW24	0.954	0.543	0.579
HW01	0.255	0.069	1.062	H112	0.881	0.498	-0.017
H121	0.514	0.097	0.307	H122	1.021	0.540	0.104
H131	0.414	0.221	0.225	H132	1.005	0.527	0.242
H141	0.493	0.242	0.057	H142	0.822	0.652	0.148
H211	0.959	0.114	0.098	H212	0.915	0.236	0.211
H221	1.029	0.209	0.230	H222	0.873	-0.024	0.162
H231	0.881	0.235	0.337	H232	0.716	-0.036	0.088
H241	0.690	0.176	0.291	H242	0.644	0.195	0.083
H311	0.632	0.294	0.203	H312	0.662	0.357	-0.127
H321	0.840	0.353	0.235	H322	0.663	0.617	-0.126
H331	0.914	0.359	0.054	H332	0.665	0.712	0.013
H341	0.804	0.277	-0.054	H342	0.670	0.495	0.105
HWBr	0.171	0.087	0.995	HW1W	1.001	0.534	0.542
				HW23	0.984	0.410	0.591

II. Phenacylidene tris(morpholino)phosphorane monohydrate, $(\text{O}(\text{CH}_2\text{CH}_2)_2\text{N})_3\text{-PCHC}(\text{O})\text{C}_6\text{H}_5 \cdot \text{H}_2\text{O}$. M.p. 146 °C. Monoclinic, $a=16.419(5)$ Å; $b=8.659(2)$ Å; $c=16.411(4)$ Å; $\beta=115.16(2)^\circ$; $V=2111.9$ Å³ ($t=-130$ °C); $M=409.46$; $Z=4$; $F(000)=912$; $D_x=1.228$ g cm⁻³. Absent reflections: $(h0l)$ for $h+l$ odd, $(0k0)$ for k odd. Space group $P2_1/n$ (No. 14).

STRUCTURE DETERMINATIONS

Both structures were determined by direct methods using the program assembly MULTAN 80 and refined in the way described in Ref. 6. It turned out that the water molecule in II was disordered in the crystal. It was possible, however, to separate the atoms into two discrete "half" molecules, OW1 and OW2; in OW1 with one hydrogen bonding to the other water molecule and in OW2 with one hydrogen bonding to a morpholino oxygen. In both molecules the second hydrogen bonding was directed toward the carbonyl oxygen, O4.

The refinements converged to conventional R -factors of 0.065(I) and 0.040(II); the R_w -values were 0.055(I) and 0.041(II). The standard deviation of an observation of unit weight, $[\sum w\Delta F^2/(m-n)]^{1/2}$, was 2.14(I) and 2.07(II). The overdetermination ratios were 8.4(I) and 7.8(II).

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

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

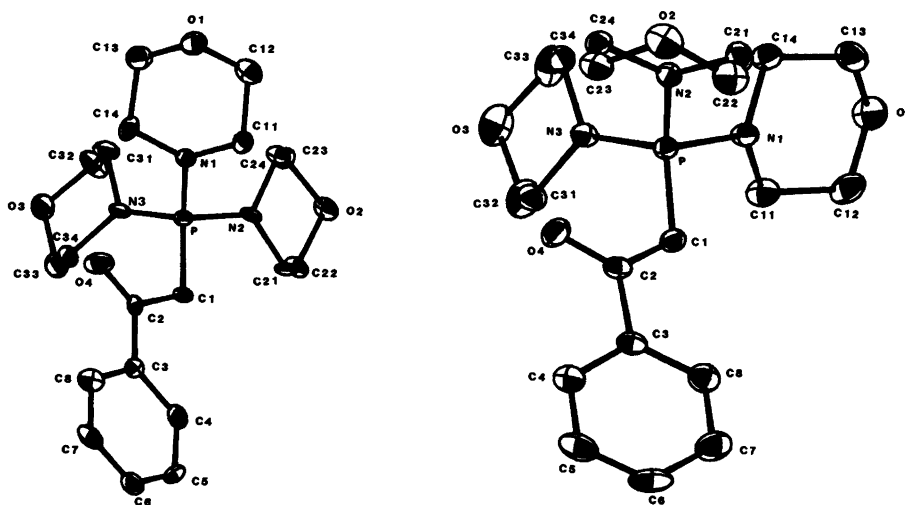


Fig. 1. ORTEP drawings of phenacyl tris(morpholino)phosphonium bromide monohydrate, I, and phenacylidene tris(morpholino)phosphorane monohydrate, II.

RESULTS AND DISCUSSION

Conformational considerations. Newman projections of the P–N and P–C bonds for the two molecules are shown in Fig. 2. The substituents linked to the central P-atom have approximately the same direction in the two compounds. Both compounds have one nitrogen atom, N1 in I and N2 in II, for which the direction of the lone pair is nearly *antiperiplanar* to the P–C bond. The direction of the lone pair of the remaining two nitrogen atoms is nearly orthogonal to the P–C1 bond.

Table 2. Structural data.

Bond lengths (Å)

		(I)	(II)			(I)	(II)
P	C1	1.791(6)	1.717(2)	O1	C13	1.438(8)	1.428(3)
P	N1	1.644(5)	1.668(2)	C13	C14	1.514(8)	1.509(3)
P	N2	1.630(5)	1.645(2)	C14	N1	1.479(7)	1.475(3)
P	N3	1.608(5)	1.641(2)	N2	C21	1.478(7)	1.471(3)
O4	C2	1.217(7)	1.258(3)	C21	C22	1.510(9)	1.515(3)
C1	C2	1.516(8)	1.399(3)	C22	O2	1.445(7)	1.425(3)
C2	C3	1.488(8)	1.513(3)	O2	C23	1.433(7)	1.425(3)
C3	C4	1.400(8)	1.397(3)	C23	C24	1.494(8)	1.509(3)
C3	C8	1.397(8)	1.388(3)	C24	N2	1.483(7)	1.479(3)
C4	C5	1.407(8)	1.383(3)	N3	C31	1.499(7)	1.463(3)
C5	C6	1.366(8)	1.380(4)	C31	C32	1.493(10)	1.506(3)
C6	C7	1.381(9)	1.381(4)	C32	O3	1.420(7)	1.437(3)
C7	C8	1.376(8)	1.392(3)	O3	C33	1.440(7)	1.423(3)
N1	C11	1.476(8)	1.474(3)	C33	C34	1.482(9)	1.508(4)
C11	C12	1.513(8)	1.508(3)	C34	N3	1.486(7)	1.472(3)
C12	O1	1.432(8)	1.425(3)				

Bond angles (°)

C1	P	N1	116.0(3)	106.0(1)	N1	C11	C12	108.2(5)	109.3(2)
C1	P	N2	104.3(3)	117.9(1)	C11	C12	O1	110.9(5)	111.7(2)
C1	P	N3	109.0(3)	112.0(1)	C12	O1	C13	110.6(5)	109.8(2)
N1	P	N2	103.8(2)	103.1(1)	O1	C13	C14	110.2(5)	111.4(2)
N1	P	N3	106.5(3)	113.8(1)	N1	C14	C13	109.0(5)	108.8(2)
N2	P	N3	117.5(3)	104.1(1)	P	N2	C21	125.4(4)	121.6(1)
P	C1	C2	115.7(4)	120.1(2)	P	N2	C24	123.3(4)	122.6(1)
O4	C2	C1	121.9(5)	123.5(2)	C21	N2	C24	110.7(4)	111.6(2)
O4	C2	C3	121.4(5)	117.0(2)	N2	C21	C22	111.3(5)	111.6(2)
C1	C2	C3	116.6(5)	119.5(2)	C21	C22	O2	111.4(5)	111.3(2)
C2	C3	C4	122.6(5)	117.9(2)	C22	O2	C23	108.1(4)	109.7(2)
C2	C3	C8	118.3(5)	123.8(2)	O2	C23	C24	111.3(5)	111.5(2)
C4	C3	C8	119.1(5)	118.3(2)	N2	C24	C23	110.9(5)	110.8(2)
C3	C4	C5	119.3(6)	120.6(2)	P	N3	C31	121.2(4)	124.6(1)
C4	C5	C6	120.4(6)	120.5(2)	P	N3	C34	128.8(4)	122.9(1)
C5	C6	C7	120.4(6)	119.6(2)	C31	N3	C34	110.0(5)	112.1(2)
C6	C7	C8	120.4(6)	120.1(2)	N3	C31	C32	110.3(5)	109.4(2)
C3	C8	C7	120.5(6)	120.8(2)	C31	C32	O3	110.7(6)	111.1(2)
P	N1	C11	122.1(4)	118.5(1)	C32	O3	C33	109.7(5)	109.5(2)
P	N1	C14	123.7(4)	121.3(1)	O3	C33	C34	112.7(5)	111.3(2)
C11	N1	C14	111.2(5)	108.9(2)	N3	C34	C33	109.9(5)	110.1(2)

Table 2. Continued.

Torsion angles (°)						(I)				
C1	P	N1	C11	70.6(5)	53.2(2)	N1	P	N3	C31	53.9(5)
C1	P	N1	C14	-88.0(5)	-167.4(2)	N1	P	N3	C34	-126.5(5)
N2	P	N1	C11	-43.1(5)	177.6(2)	N2	P	N3	C31	-61.9(5)
N2	P	N1	C14	158.3(5)	-42.9(2)	N2	P	N3	C34	117.7(5)
N3	P	N1	C11	-167.8(4)	-70.3(2)	N1	P	C1	C2	51.2(5)
N3	P	N1	C14	33.6(5)	69.1(2)	N2	P	C1	C2	164.7(4)
C1	P	N2	C21	24.6(6)	66.4(2)	N3	P	C1	C2	-69.0(5)
C1	P	N2	C24	-165.5(5)	-88.8(2)					
N1	P	N2	C21	146.5(5)	-49.9(2)					
N1	P	N2	C24	-43.6(5)	154.9(2)					
N3	P	N2	C21	-96.2(5)	-168.9(2)					
N3	P	N2	C24	73.6(5)	36.0(2)	N1	P	N3	C31	108.4(2)
C1	P	N3	C31	179.8(11)	-11.8(2)	N1	P	N3	C34	-64.5(2)
C1	P	N3	C34	-0.6(6)	175.4(2)	N2	P	N3	C31	-140.2(2)
						N2	P	N3	C34	47.0(2)
						N1	P	C1	C2	175.7(2)
						N2	P	C1	C2	61.0(2)
						N3	P	C1	C2	-59.7(2)

Various derived and averaged data

Nx	(I)			(II)		
	N1	N2	N3	N1	N2	N3
$\overline{N-C}$ (Å)	1.478	1.481	1.493	1.475	1.475	1.468
$\overline{C-C}$ (Å)	1.514	1.503	1.488	1.509	1.512	1.507
$\overline{C-O}$ (Å)	1.435	1.439	1.430	1.427	1.425	1.430
Sum of Nx bond angles (°)	357.0	359.4	360.0	348.7	355.8	359.6
Torsion angle						
C1–P–Nx–Lone pair(N) (°)	171.3	-70.5	89.6	-57.1	168.8	81.8
Sum of NPN angles (°)		327.8			321.0	
Sum of CIPN angles (°)		329.3			335.0	
Sum of NPX angles, X=N, Cl (°)	325.5	325.6	330.0	322.9	325.1	329.9

In the phosphonium cation all nitrogen atoms are nearly sp^2 -hybridized; the sum of the angles around the nitrogen atoms varying from 357 to 360°. In the phosphorane, however, one of the nitrogen atoms, N1, has a high degree of sp^3 -hybridization, $\Sigma < N1 = 348.7^\circ$, while the two other nitrogen atoms are essentially sp^2 -hybridized, $\Sigma < N2 = 355.8^\circ$ and $\Sigma < N3 = 359.6^\circ$. The presence of one nitrogen atom being partly sp^3 -hybridized and two nitrogen atoms being nearly sp^2 -hybridized is in agreement with the results obtained in earlier structural studies of compounds with three P–N bonds.^{4,6,7} However, contrary to what has been observed in previous structural studies of this class of compounds it is not the nitrogen atom of highest sp^3 character in II, N1, which has its lone pair *antiperiplanar* to the P–C1 bond but atom N2.

When looking at the N–P–N bond angles it is clear that the molecules are highly asymmetrical. In both compounds there are two small and one large bond angles, the

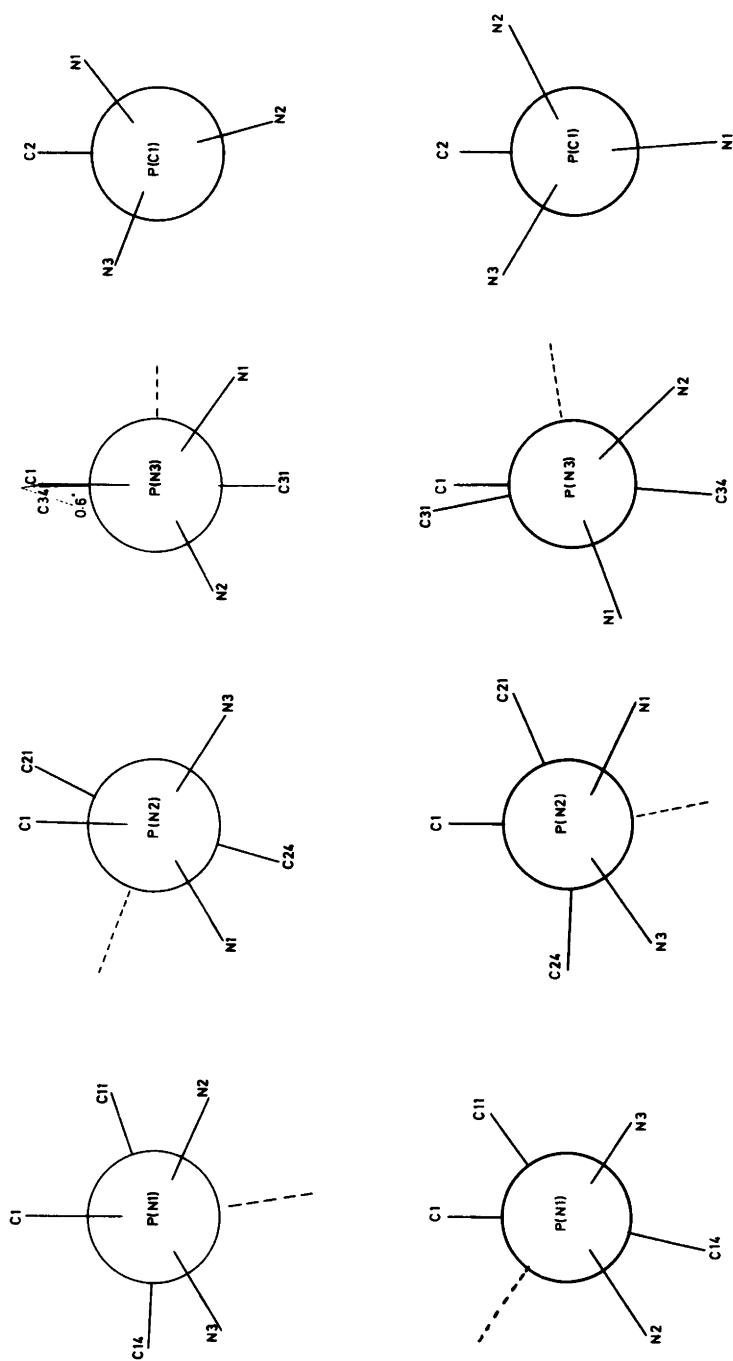


Fig. 2. Newman projections along P–N and P–C bonds.

difference being 10–14°. In both compounds it is the nitrogen atom which has its lone pair *antiperiplanar* to the P–C1 bond which has two small adjacent bond angles. For the N–P–C1 bond angles there exists no clear pattern; all the bond angles are significantly different from each other. It is apparent, however, that in both compounds it is the nitrogen atom with its lone pair *antiperiplanar* to the P–C1 bond which has the greatest N–P–C1 bond angle.

Phosphorus-nitrogen bond lengths. In earlier structural studies on tervalent and pentavalent species the P–N bond lengths have been found to be in the 1.63–1.73 Å range. All bond lengths may in principle be considered as P–N single bond lengths, although Scherer *et al.*¹¹ in a recent study have reported a P–N single bond of 1.771(4) Å in a P^{III} compound. The variations in the P–N single bond lengths seem to be caused by a number of factors; the charge of the phosphorus atom,⁴ the electronegativity of the substituents⁷ and finally the torsion angle of the P–N bond with its consequences for the hybridization of the nitrogen atoms.⁶

In the present compounds the P–N bond lengths range from 1.608(5) to 1.644(5) Å in I and from 1.641(2) to 1.668(2) Å in II. The P–N bond lengths in I are comparable with those previously observed in 4-nitrobenzyl tris(morpholino)phosphonium perchlorate.⁴ The average P–N bond length in II is considerably shorter than in the parent phosphine, Mor₃P,⁶ and is also slightly shorter than in Mor₃PX (X=O, Se and Te). The longest P–N bond in the phosphonium cation is observed for the nitrogen atom with its lone pair *antiperiplanar* to the P–C1 bond. This observation is in agreement with earlier structural studies.^{4,6,7} In II, however, the longest P–N bond is to the nitrogen atom of highest *sp*³ character which is not the one with its lone pair being *antiperiplanar* to the P–C1 bond as mentioned above. Apparently, the hybridization of the nitrogen atom is more important to the P–N bond length than is the direction of the nitrogen lone pair.

In the phosphonium cation the two short P–N bond lengths to the nitrogen atoms having their lone pair orthogonal to the P–C1 bond are probably significantly different, P–N2 and P–N3 being 1.630(5) Å and 1.608(5) Å, respectively. It is notable that the sum of the NPX (X=N and C1) bond angles for atom N3 is considerably greater than for atom N2, *cf.* last entry in Table 2. This may suggest that the steric conditions for these two nitrogen atoms are different and may influence the P–N bond lengths.

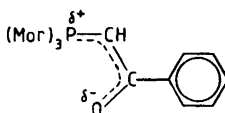
In the phosphorane, II, there is one P–N bond (P–N1=1.668(2) Å) which is significantly longer than the other two (P–N2=1.645(2) Å and P–N3=1.641(2) Å). When considering the lone pair directions one will find that for the long P–N1 bond the torsion angle between the phosphorus-carbon bond and the direction of the lone pair of N1 is only –57.1°. For one of the short bonds, P–N2, however, the nitrogen lone pair is *antiperiplanar* to the P–C1 bond. From this result it appears that the direction of the lone pair of the nitrogen atoms relative to the P–C1 bond has no dominating effect on the P–N bond lengths as mentioned above.

Phosphorus-carbon bond lengths. The P–C(alkyl) bond length is known to fall in the 1.78–1.83 Å range and not to be significantly dependent on the nature of the alkyl group. In I the P–C1 bond length is 1.791(6) Å, and thus is of the same order of magnitude as the P–C bond length in structurally similar compounds as 4-nitrobenzyl tris(morpholino)phosphonium perchlorate, 1.809(2) Å, 4-nitrobenzyl tris(piperdino)phosphonium perchlorate, 1.813(3) Å,⁴ and Ph₃P⁺–CH₂C(O)CH₂Cl Cl[–], 1.795 Å.¹² This resemblance in the P–C bond lengths suggests that the P–C bond in I is a pure single bond without any delocalization of electron density from the phenacyl substituent to the positively charged phosphorus atom.

The P=C bond length may range from 1.69 to 1.58 Å, depending upon the hybridization and the coordination number of the phosphorus atom and upon the substituents. In II the P=C1 bond length is 1.717(2) Å and is, within the limit of error, equal to 1.71 Å as observed in $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{Ph}$.⁵ For other tetracoordinated pentavalent phosphorus compounds, the following P=C bond lengths have been found: $\text{Ph}_3\text{P}=\text{C}(\text{CH}_2)_3$ 1.668(3) Å,¹³ $((\text{Me}_2\text{N})_3\text{P})_2=\text{C}$ 1.58(1) Å,³ and $(\text{Me}_3\text{P})_2=\text{C}$ 1.594(3) Å.¹⁴ These results and the fact that the difference between the length of a X-C single bond and a X=C double bond is fairly constant, approximately 0.20 Å, indicate that the P-C1 bond in II is long and cannot be characterized as a pure P=C double bond.

The C1-C2 bond length of 1.516(8) Å in I and 1.399(3) Å in II are similar to a C-C single bond and a delocalized aromatic C-C bond, respectively.

The C=O bond length in phenacyl compounds are generally fairly constant within the 1.215–1.225 Å range.^{15–18} In I the C=O bond of 1.217(7) Å falls within these limits. In II the C=O bond length is 1.258(3) Å and is therefore significantly different from the normal C=O bond lengths but is similar to what has been observed in $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{Ph}$, 1.26 Å.⁵ This elongation of the C=O bond is also confirmed by the infrared spectrum (KBr), where the C=O stretching frequency is observed at 1520 cm^{-1} . The reason for this elongation of the C=O bond may be due to two factors; the first and probably the most dominating one is transfer of electron density from the phosphorus atom through the conjugated C1-C2 bond to the electronegative oxygen atom resulting in a positive charge on the phosphorus atom and a negative charge on the oxygen atom, *cf.* Scheme 2. The second factor which may influence the bond length is the hydrogen bond to the water molecule and possibly to the *ortho*-hydrogen atom of the phenyl ring.



Scheme 2.

The phosphorus-phenacyl part of the molecules. In the phosphonium cation this part is nearly planar; the distance from the plane through all non-hydrogen atoms to the various atoms is within 0.03 Å. In II, however, the torsion angles O4-C2-C3-C4 and C1-C2-C3-C4 are 16.1 and -164.0° , respectively, which indicate that the P-C1-C2-O4 part of the substituent is turned out of the plane of the phenyl ring.

The $\text{P}^+-\text{C1}-\text{C2}$ bond angle in I, $115.7(4)^\circ$, is significantly greater than the tetrahedral angle, and may be one of the reasons why the methylene hydrogens are acidic. This high acidity is demonstrated by the facile synthesis of II from I with NaHCO_3 , and by the observation that one of the hydrogen atoms is hydrogen bonded to the water molecule. In the phosphorane the $\text{P}=\text{C1}-\text{C2}$ bond angle is $120.1(2)^\circ$ which is as expected for an sp^2 -hybridized carbon atom.

In both compounds the C2 atom has highly asymmetrical bond angles. In I the C1-C2-C3 bond angle is the smallest one, $116.6(5)^\circ$, while the O4-C2-C1 and O4-C2-C3 bond angles are greater than 120° , $121.9(5)^\circ$ and $121.4(5)^\circ$, respectively. In 2-phenylsubstituted 1-ethanones, phenacyl compounds, this pattern with regard to the bond angles around the carbonyl carbon atom seems to be quite general.¹⁷ In II, however, the O4-C2-C3 bond angle is the smallest one, $117.0(2)^\circ$. The decrease of this angle may again be attributed to the effect of the transfer of electron density from the phosphorus atom to the C1 atom.

Morpholino substituents. The bond distances and the bond angles in these groups are listed in Table 2. They are all within the expected range. In both compounds the morpholino substituents have the chair conformation, and in I they are linked equatorially to the central phosphorus atom. In the phosphorane, II, however, one of the morpholino groups, the one containing N2, is connected axially to the central atom.

Water molecules. Both compounds contain one molecule of crystal water. In the phosphonium salt, I, the water molecule has three contacts well within the sum of the van der Waals' radii of the involved atoms. One of the hydrogen atoms, HWO1, points toward O1 in one of the morpholino groups, while the other hydrogen atom, HWBr, is oriented toward the bromide ion; the H–O and H–Br distances being 2.093 and 2.532 Å, respectively. The corresponding bond angles are O1–HWO1–OW, 178.1° and Br–HWBr–OW, 163.1°. The third contact is between one of the lone pairs on the water oxygen atom and one of the methylene hydrogen atoms, H11, with a H11–OW distance of 2.032 Å and a C1–H11–OW bond angle of 162.8°.

In the phosphorane, II, the water molecule is disordered and of the four water molecules in the unit cell two and two are interconnected through a hydrogen bond. The distance between the two half molecules, OW1 and OW2 in the asymmetrical unit is 0.785 Å, and between OW1 and OW2' in the next asymmetrical unit is 2.902 Å. OW1 has two hydrogen bonds, one to OW2' and one to the carbonyl oxygen atom, O4, with O4–HW14 and OW2'–HW1W bond distances of 1.992 and 2.069 Å, respectively. The OW1–HW14–O4 and OW2'–HW1W–OW1 bond angles are 171.9 and 158.3°. The other half, OW2, has contacts to O4, HW24–O4=2.180 Å, and to an oxygen atom of one of the morpholino groups, O3, HW23–O3=2.379 Å. The oxygen atom in OW2 may therefore be considered as being three-coordinated. The corresponding bond angles, O4–HW24–OW2 and O3–HW23–OW2, are 141.5 and 158.6°, respectively.

The results from the X-ray study are in accordance with the IR spectra; in both compounds two strong and sharp bands are observed in the 3300–3500 cm⁻¹ region. The position and the sharpness of the bands indicate that the hydrogen bonds are weak. The observation that the methylene hydrogen atom in I takes part in a hydrogen bonding interaction is understandable in view of the fact that phenacylphosphonium salts are quite acidic compounds owing to the strongly activating groups adjacent to the methylene carbon atom.¹⁹ It is notable that it is one of the oxygen atoms belonging to a morpholino group which takes part in one of the hydrogen bondings in I and not the carbonyl oxygen atom which is supposed to be the better donor. Presumably this preference for the morpholino oxygen atom is due to packing effects in the crystal lattice.

¹³C chemical shifts. The ¹³C chemical shifts together with the ¹³C–³¹P coupling constants for the phosphonium salt, I, the phosphorane, II, and for the corresponding compounds derived from Ph₃P from Ref. 20, are listed in Table 3. The assignment of the peaks was based upon the multiplicity and the intensity of the signals, on the long range P–C couplings and from a comparison with results from NMR-studies on similar compounds.^{20,21}

For the morpholino groups the chemical shifts are within 1 ppm equal to the shifts observed for Mor₃P and Mor₃P=X (X=O,S,Se and Te).²² This indicates that the chemical shifts of the carbon atoms in the morpholino groups are quite insensitive to the hybridization of the phosphorus atom. There seems to be no obvious correlation between the slightly different shifts and the P–N bond lengths or the hybridization of the nitrogen atoms as viewed by the sum of the nitrogen bond angles.

For the phenacyl groups the differences in the chemical shifts are likewise quite small. The most significant variations are observed for the carbonyl carbon atom, C2. In the Acta Chem. Scand. A 39 (1985) No. 8

Table 3. ^{13}C NMR chemical shifts (ppm from TMS) and ^{13}C - ^{31}P coupling constants (Hz) in the parentheses for phosphonium salts and phosphoranes derived from Mor_3P and Ph_3P .

Compound	C2	C1	C-N-C	C-O-C	C_{ipso}	C_{ortho}	C_{meta}	C_{para}
$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{2}}{\text{CH}_2}-\overset{\text{+}}{\text{P}}\text{Mor}_3$	193.63 (5.5)	^a	45.96	66.98 (5.2)	136.94 (8.2)	130.20	129.77	135.44
$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{2}}{\text{CH}_2}-\overset{\text{+}}{\text{P}}\text{Ph}_3^b$	191.4 (7.0)	38.8 (62.5)			^a	129.9	128.9	134.7
$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{PMor}_3$	184.33 (5.7)	52.97 (167.9)	46.25	67.62 (5.5)	143.65 (18.6)	128.58	127.36	129.79
$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{PPh}_3^b$	184.9 (3.0)	50.4 (111.7)			141.4 (15.0)	127.7	127.0	129.3

^a Insufficient signal-to-noise ratio to be assigned. ^b From Ref. 20.

phosphorane this carbon atom is shielded as compared with the corresponding atom in the phosphonium cation in both series: *cf.* Table 3. The difference in the shift for this atom amounts to -9.3 ppm for the compounds derived from Mor_3P and -6.5 ppm for the corresponding compounds containing PPh_3 . Provided this difference can be taken as a measure for the stabilization of the ylide due to the resonance structure depicted by $\text{P}^{\delta+}-\text{C}=\text{C}-\text{O}^{\delta-}$, as shown in Scheme 2, these values and the corresponding difference for the shifts in the compounds derived from Ph_3As ,²⁰ -11.0 ppm, suggest this stabilization to increase in the order $\text{Ph}_3\text{P} < \text{Mor}_3\text{P} < \text{Ph}_3\text{As}$. The chemical shifts for the phosphoranes may separately indicate the same order. It should be emphasized, however, that the contribution of the ylidic form of the phosphoranes must be highly limited since the considerable coupling constants for the phosphoranes indicate that the C1 atom is approximately sp^2 -hybridized.

The NMR-results seem to indicate that the reactivity of II will be somewhat higher than that of the corresponding phosphorane derived from Ph_3P but less than that of the corresponding arsorane. This conclusion is in agreement with Issleib's original suggestion.² No Wittig reactions or similar reactions involving phosphoranes derived from aminophosphines seem to have been performed which could confirm this difference in reactivity. This difference is not sufficiently large to be detected by X-ray studies of the two types of compounds.

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