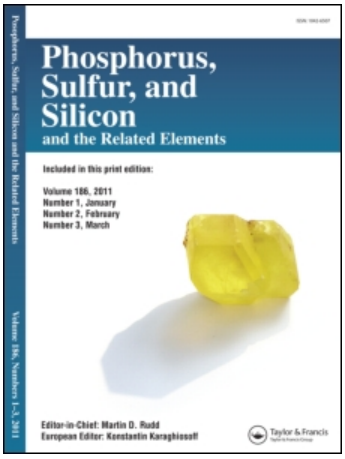

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ALKYL PHOSPHAZINES, $(C_6H_5)_3PNNC(R_1)(R_2)$: [*i*) $R_1=CH_3$; R_2=*i-Bu* AND *ii*) $R_1=R_2=C_6H_5CH_2$]. SYNTHESIS, CONVERSION TO METHYL IODIDE SALT AND SINGLE CRYSTAL X-RAY STRUCTURE OF PHOSPHAZINIUM BROMIDE, $[(C_6H_5)_3P=N(H)N=C(CH_3)(i\text{-}Bu)]$ B*r*

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Two new examples of alkyl triphenylphosphazinium bromides have been prepared and characterised. Contrary to earlier practice, these salts have been effectively dehydrobrominated by the use of triethylamine. Excess of methyl iodide in its reaction with phosphazine afford only mono methylation, occurring at phosphinimino nitrogen. ^{31}P chemical shifts of several phosphazinium bromides measured in this study show a much smaller variation (35–38 δ) compared to their free bases (14–20 δ). The first single crystal X-ray structure of β-N (methyl, isobutyl) triphenylphosphazinium bromide (**1a**) reveals the presence of i) nearly unaffected N-N bond distance and ii) hydrogen bonding with the bromide ion.

Keywords: Triphenyl phosphazinium ion and alkyl phosphazines; mono methylation; ^{31}P-nmr; X-ray structure

INTRODUCTION

Phosphazines, $R_3P{=}N\text{-}N{=}CR_1R_2$ are novel class of compounds possessing both phosphinimino ($R_3P{=}N$-) and ketimino ($R_2C{=}N$-) groups linked through

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N-N bond. While the chemistry of phosphinimines (> P═N-R) and ketimines (or aldimines) (>C═N-R) are well developed, that of phosphazine is less known[1], though the very first phosphazine was reported as early as in 1919[2].

In general, phosphazinium salts are stable to permit both their isolation and storage unlike phosphazines, which show high degree of sensitivity to moisture attack at P═N bond. Walker's method[3], the latest of three methods developed for their synthesis still stands superior by virtue of its simplicity and general applicability. Surprisingly, no new examples of alkyl phosphazines or their salts have been made since 1965. We report in this paper, (i) synthesis of two new alkyl phosphazines as their HBr salts, (ii) conversion of these to the free bases by using $(C_2H_5)_3N$, (iii) mono methylation of the free bases, (iv) ^{31}P NMR chemical shifts of various phosphazinium salts and their free bases and (v) the first single crystal X-ray structure of one of the phosphazinium salts synthesized in this study.

RESULTS AND DISCUSSION

N-amino phosphiniminium bromide (**1A**) reacts smoothly with methyl isobutyl ketone and dibenzyl ketone to afford HBr salt of the corresponding phosphazine in about 90 per cent yield.

$$(C_6H_5)_3P{=}N\text{-}NH_2.HBr + (R_1)CO(R_2) \xrightarrow[-H_2O]{} (C_6H_5)_3P{=}N\text{-}N{=}C(R_1)(R_2).HBr$$

(1A)

(i) $R_1 = CH_3$; $R_2 = i\text{-}C_4H_9$ (**1a**)

(ii) $R_1 = R_2 = C_6H_5CH_2$- (**2a**)

While different reagents such as sodamide in liquid ammonia[4], n-BuLi[5], magnesium hydride[6], lead tetraacetate[7] etc., have been employed for the dehydrohalogenation studies of phosphinimium halides, $[R_3PN(H)R]^+ X^-$, aqueous alkali extraction[8] and column chromatography over basic alumina[3] were satisfactory for the generation of free phosphazines from their salts. We found room temperature stirring of the slurry of phosphazinium salt in C_6H_6 or CCl_4 in presence of $(C_2H_5)_3N$ being quite effective in releasing the free phosphazine. This has been proved by both derivatization of the free phosphazine with methyl iodide and ^{31}P NMR spectroscopy (Table I).

TABLE I ^{31}P Chemical shifts of phosphazinium salts (**a**) and their free bases (**b**)

Compound No.*	R_1	R_2	^{31}P (δ *in ppm*)	
			HBr salt (a)	*Free base (b)*
1#	CH_3	i-Bu	37.5	14.7
2#	$C_6H_5CH_2$	$C_6H_5CH_2$	37.8	15.2
3.	H	$(CH_3)_2CH$	35.1	13.9
4.	$-(CH_2)_5-$		37.3	14.0
5.	CH_3	C_6H_5	38.1	15.5
6.	H	C_6H_5	37.2	18.2
7.	C_6H_5	C_6H_5	38.0@	15.9
8.	H	p-$(NO_2)C_6H_4$	37.2	19.7

*Compounds 3 to 8 (a&b) were synthesized by following literature methods[3,10a]. M.pt and CHN analysis of our samples were in good agreement with the reported values.
#New phosphazines synthesized in this study.
@isolated in 60% yield by us. Walker et al[3] could not isolate.

Changing R groups in phosphazine is found to exert only moderate influence on the phosphorus chemical shift (14–20 δ) in contrast to significant chemical shift differences observed with changing group on nitrogen of phosphinimines (> P═N-R)[1]. Expectedly, phosphorus in the phosphazinium salts experiences more deshielding (about 20 ppm shift) compared to the corresponding free phosphazine. The trend is very similar to that observed in the case of Ph_3PNNH_2 **(1B)** (δ ^{31}P: 18 ppm) and its HBr salt **(1A)** (δ ^{31}P: 38 ppm). Interestingly, we observe in case of compounds $[(C_6H_5)_3P{=}N(CH_3)N{=}C(CH_3)(i\text{-}Bu)]^+I^-$ and $[(C_6H_5)_3P{=}N(CH_3)N{=}C(CH_2C_6H_5)_2]^+I^-$ further deshielding of phosphorus upon methylation at the phosphinimino nitrogen.

Proton attached to phosphinimino nitrogen in these salts appear as highly deshielded doublet (δ 10–12 ppm) due to phosphorus coupling ($^2J_{P\text{-}H}$: 16–23 Hz). Basicity of phosphinimino nitrogen is known to be more than that of ketimino nitrogen[9a–c] and hence only mono hydrogen halide salt of phosphazines could be prepared[2,3,10]. We did not observe any methylation of ketimino nitrogen in spite of having inductively electron releasing alkyl groups and imposing fairly drastic reaction conditions.

X-RAY STRUCTURE

Single crystal X-ray structural study on any example of a phosphazine or its salt has not been reported so far. Thus, the X-ray structure of $[(C_6H_5)_3P{=}N(H)N{=}C(CH_3)(i\text{-}Bu)]^+\ Br^-$ **(1a)** reported here is the first example of such a study. Crystallographic data for **1a** are given in Table II. ORTEP

TABLE II Crystallographic data for $[(C_6H_5)_3P{=}N(H)N{=}C(CH_3)(i\text{-}Bu)]^+ Br^-$ (**1a**)

Molecular formula, M·Wt.	:	*$C_{24}H_{28}N_2PBr$; 455.36*
Unit cell dimensions	:	a = 9.082(2)A°;b = 9.114(3)A°; c = 14.509(5)A°;α = 85.09(2)°; β = 80.00(3)°;γ = 82.84 (2)°; V = 1171.0(6)A°^{3};z = 2.
Calculated density	:	1.291 mg/m^3
Crystal system, space group	:	Triclinic, $P\bar{1}$
# of reflections observed	:	4395
# of unique reflections	:	2153
Criteria observed	:	$I \geq 3\sigma(I)$
Program used for structure solution	:	SHELXS-86
Program used for structure refinement	:	SHELXL-93
Final R Index	:	0.032
WR2	:	0.072
GOF	:	1.079
Max. and Min. electron density in the final difference map	:	6-0.27 E/Å^3

plot and selected bond length and bond angle data are given in Figure 1 and Table III respectively. Different structural alternatives theoretically possible for the protonated phosphazine are given in Scheme 1. X-ray structure proves protonation occurring at phosphinimino nitrogen (**A**). It is also seen that this proton is involved in hydrogen bonding with bromide which is the counter ion. The N1-H distance is considerably shortened (obs. 0.81 Å; exp. 1.02 Å[18]) revealing the strong basic nature of the phosphinimino nitrogen N1. The hydrogen bond in N-H...Br which is bent by about 10° has a distance of 3.305 Å, which is shorter by about 0.15 Å compared to their van der Waals contact[18]. Expectedly, nitrogen N1 reveals pyramidal character unlike N2 which is nearly planar. Both N-N and N-C bond lengths are relatively unaffected from the expected values (1.40 Å and 1.28 Å respectively)[11], whereas the P-N bond shows a noticeable change (1.55 Å[12] to 1.64 Å) which is presumably due to protonation. Phosphorus assumes an approximately tetrahedral geometry where as the carbon atom carrying methyl and isobutyl substituents is planar as expected. No new feature is seen with the phenyl and alkyl substituents. It could be safely said that the bromide ion is neither in contact with ketimino nitrogen nor involved in extended hydrogen bonding interaction with neighbouring molecules as the distance of N2...Br is 4.021 Å in comparison to their van der Waals contact (3.450 Å)[18].

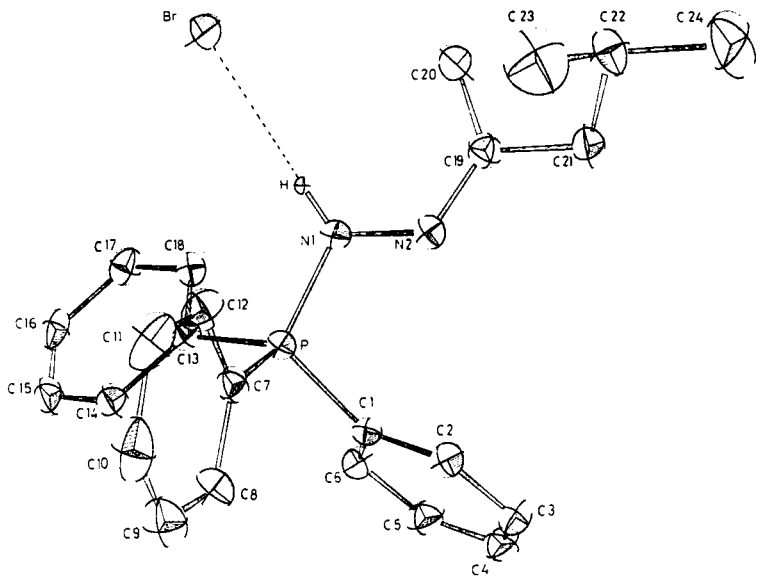
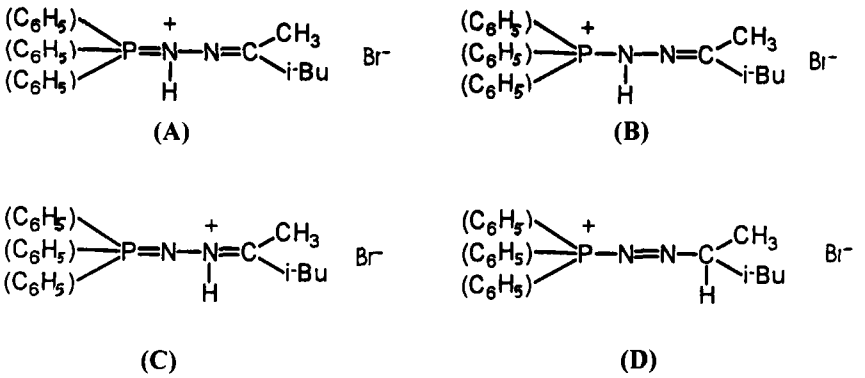


FIGURE 1 ORTEP diagram for $[(C_6H_5)_3P{=}N(H)N{=}C(CH_3)(i\text{-}Bu)]^+ Br^-$ (**1a**).

TABLE III Selected bond lengths (A°) and bond angles (deg) for $[(C_6H_5)_3P{=}N(H)N{=}C(CH_3)(i\text{-}Bu)]^+ Br^-$ (**1a**)

Bond lengths: (Å)			
P-C1	1.797(3)	C19-C20	1.490(6)
P-C7	1.781(4)	C19-C21	1.492(5)
P-C13	1.785(4)	C21-C22	1.526(6)
P-N1	1.612(3)	C22-C23	1.519(8)
N1-N2	1.427(4)	N1-H28	0.815
N2-C19	1.283(4)	H28-Br	2.499
		N1-H...Br	3.305(7)
Bond angles: (°)			
N1-P-C7	114.3 (2)	N1-H...Br	170.5
N1-P-C13	105.6(2)	N2-C19-C20	125.5(4)
C7-P-C13	109.6 (2)	N2-C19-C21	116.1(4)
N1-P-C1	107.4(2)	C20-C19-C21	118.5(4)
C7-P-C1	109.8(2)	C19-C21-C22	114.1(4)
C13-P-C1	110.0(2)	C23-C22-C24	112.7(6)
N2-N1-P	112.3(2)	C21-C22-C24	111.2(5)
C19-N2-N1	115.2(3)	C21-C22-C23	109.6(5)



SCHEME 1

EXPERIMENTAL

X-ray Measurements

The intensities for structure (**1a**) were collected on CAD–4 Enraf-Nonius Diffractometer using Mo K_α radiation (λ = 0.71073 Å). Lattice parameters and their standard deviations were obtained by least square refinement of 25 carefully selected reflections in the θ range 8–14°. A total of 4395 reflections were measured, of which 2313 reflections were observed with $I \geq 3\sigma(I)$ and 2153 unique reflections were used for structure analysis. The structure was solved by Heavy atom method. Br and P positions were obtained from the Patterson map (SHELXS-86)[14] and the successive Fourier maps based on Br and P positions, have revealed the positions of remaining non-hydrogen atoms of the molecule. The positional parameters and isotropic thermal parameter of all the non-hydrogen atoms were refined with full matrix least-squares method using the program SHELXL-93[15] followed by an anisotropic temperature factors. All the hydrogen atoms were located from the difference electron density maps during the course of the refinement and their positional parameters along with isotropic temperature factors were refined.

Solvents, Reagents and General Procedures

Standard procedures[13] were employed to purify and dry the necessary solvents, CH_3I (S.D.) and $(C_2H_5)_3N$ (S.D.), $(C_6H_5)_3P$ (Fluka) and Br_2(BDH) were used as such. Anhydrous N_2H_4 and $(C_6H_5)_3P{=}N\text{-}NH_2.HBr$ (**1A**) were prepared using the reported procedures[16,17].

New compounds were characterised on the basis of spectroscopic and analytical data IR (Perkin Elmer 1430; KBr discs), ^{1}H and ^{31}P NMR (JEOL JNM JSX; 400 MHz; TMS and H_3PO_4 (85%) are internal and external standards respectively), MS (Finnigan Mat 8230, 70 eV) and Heraeus CHN micro analyser were the instrumental facilities used.

(i) Preparation of $[(C_6H_5)_3P{=}N(H)N{=}C(CH_3)(i\text{-}Bu)]^+ Br^-$ **(1a)**

To a stirred solution of $(C_6H_5)_3P{=}N\text{-}NH_2.HBr$ **(1A)** (5.0 g, 13.4 mmol) in CH_3OH (40 ml), was added $(i\text{-}Bu)CO(CH_3)$ (1.3 g, 13.4 mmol) at room temperature (about 30 °C) in 0.5 hr. Filteration of reaction mixture after 5 hr followed by removal of methanol gave a white powdery solid, which was washed with $(C_2H_5)_2O$ and recrystallized from CH_3OH to obtain $[(C_6H_5)_3PN(H)NC(CH_3)(i\text{-}Bu)]^+ Br^-$ **(1a)** (5.3 g, 87%). m.p:189–90°C (dec); **IR** (600–1600cm^{-1}): 1574(s), 1469(m), 1427(vs), 1379(s), 1178(m), 1149(m), 1091(vs), 950(vs), 915(vs), 842(w), 806(vw), 787(w), 768(vw), 707(s), 678(vs) and 643(vs); **^{1}H NMR** ($CDCl_3$, δ in ppm): 0.75(6H,d),1.85(1H,m),2.00(2H,d),2.35(3H,s),7.56–7.90(15H,m) and 10.33(1H,d;$^{2}J_{P\text{-}H}$: 16.0 Hz); **^{31}P NMR**-{^{1}H} (CH_2Cl_2, δ in ppm); 37.5 (s); **CHN** $C_{16}H_{28}N_2BrP$ Calcd:C,63.20;H,6.15;N,6.15; Found:C,62.48; H,5.91;N,6.27.

(ii) Preparation of $[(C_6H_5)_3P{=}N(H)N{=}C(CH_2Ph)_2]^+ Br^-$ **(2a)**

Dibenzyl ketone (2.8 g, 13.4 mmol) was reacted with **(1A)** (5.0 g, 13.4 mmol) and worked up as above to obtain $[(C_6H_5)_3PN(H)NC(CH_2C_6H_5)_2]^+ Br^-$ **(2a)** as an yellow oil (6.2 g, 81%). **IR** (600–1600 cm^{-1}):1596(s), 1491(s), 1442(vs), 1393(vs), 1320(m), 1198(w), 1182(w), 1123(vs), 1064(w), 1039(s), 1002(s), 958(m), 860(w), 763(s), 738(s), 703(s) and 631(w). **^{1}H NMR** ($CDCl_3$, δ in ppm): 3.35(4H,s);7.10–8.05(25H,m);12.00(1H,d;$^{2}J_{P\text{-}H}$: 23.0 Hz) **^{31}P NMR**-{1H} (CH_2Cl_2, δ in ppm): 37.8 (s).

(iii) Preparation of $[(C_6H_5)_3P{=}N\text{-}N{=}C(H)(C_6H_4(NO_2)\text{-}p)]$ **(8b)** from its HBr salt **(8a)**.

To a stirred slurry of $[(C_6H_5)_3P{=}N\text{-}N{=}C(H)(C_6H_4(NO_2)\text{-}p)].HBr$ **(8a)** (1.0 g, 2.2 mmol) in dry C_6H_6 (20 ml), was added $(C_2H_5)_3N$ (0.20 g, 2.2 mmol) at room temperature (about 30°C) under nitrogen atmosphere. After 1 hr, $(C_2H_5)_3N.HBr$ was separated by filteration and C_6H_6 was removed from the filterate to get an orange solid which was recrystallized from C_6H_6-CH_3CN mixture to obtain orange crystals of $(C_6H_5)_3PNNC(H)(C_6H_4(NO_2)\text{-}p)$ **(8b)** (0.80 g, 95%). m.p:142–43 °C; **IR** (600–1600 cm^{-1}): 1580(m), 1500(s), 1459(vs), 1366(s), 1322(s), 1202(vw), 1096(s), 1026(vs), 940(m), 898(m), 859(m), 820(w), 742(w),

720(s) and 682(s); **^{1}H NMR** ($CDCl_3$, δ in ppm):7.25–8.15(19H,m);8.42(1H,s); **^{31}P NMR**-{1H} (C_6H_6, δ in ppm): 19.7 (s); **CHN**:$C_{25}H_{20}N_3O_2P$ Calcd:C,70.58; H,4.70;N,9.88; Found:C,70.91;H,4.22;N,10.43.

(iv) Reaction of $(C_6H_5)_3P{=}N\text{-}N{=}C(CH_3)$(i-Bu) (**1b**) with CH_3I

$(C_6H_5)_3PNNC(CH_3)$(i-Bu) (**1b**) (1.2 g, 2.7 mmol) generated from its HBr salt (**1a**) using the procedure given in (iii) was treated with excess CH_3I (1.9 g, 13.3 mmol) at room temperature. After 10 hr, the precipitate was obtained by filteration, washed with $(C_2H_5)_2O$ and recrystallised from CH_3OH to obtain white crystals of $[(C_6H_5)_3P{=}N(CH_3)N{=}C(CH_3)$(i-Bu)$]^+I^-$ (**1c**) (0.82 g, 59%). m.p:147–49°C; **IR** (600–1600 cm^{-1}): 1584(m), 1460(s), 1378(s), 1315(m), 1150(s), 1108(vs), 1064(w), 1040(w), 1022(w), 997(m), 925(m), 891(m), 760(m), 720(s) and 698(s); **^{1}H NMR** ($CDCl_3$, δ in ppm): 0.76(6H,d);1.88(1H,m); 2.01 (2H,d);2.38(3H,s);3.80(3H,d,$^3J_{P\text{-}H}$: 9.2Hz) and 7.65–7.90 (15H,m); **^{31}P NMR**-{1H} (CH_2Cl_2, δ in ppm): 44.1 (s); **CHN**: $C_{25}H_{30}N_2PI$ Calcd:C,58.13;H, 5.81;N,5.42; Found:C,57.30;H,6.27;N,5.26.

Similarly, the reaction of $(C_6H_5)_3P{=}N\text{-}N{=}C(CH_2C_6H_5)_2$ (**2b**) (2.0 g, 4.1 mmol) with CH_3I (2.9 g, 20.6 mmol) gave the analogous product $[(C_6H_5)_3P{=}N(CH_3)N{=}C(CH_2C_6H_5)_2]^+I^-$ (**2c**) (1.8 g, 66%); **IR** (600–1600cm^{-1}): 1584(m), 1456(vs), 1402(s), 1376(m), 1321(m), 1190(s), 1118(vs), 1075(m), 841(vw), 811(m), 792(m), 758(m), 720(vs) and 692(vs); **^{1}H NMR**($CDCl_3$, δ in ppm): 3.31(4H,s); 3.87(1H,d;$^3J_{P\text{-}H}$:9.0 Hz) and 7.13–8.09(25H,m); **^{31}P NMR**-{^{1}H} (CH_2Cl_2, δ in ppm): 43.6(s).

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