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Synthesis, Spectroscopic Investigation and X-ray Structural Characterization of Some Primary Ammonium Phosphine Oxide, $(R\text{-}C_6H_6NH_3^+)(^-O)P(:O)_2H$

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The synthesis and identification of the first primary ammonium phosphonate $RC_6H_4NH_3(^-O)P(:O)_2H$, where R = H, *o*-CH_3, *m*-CH_3, and *p*-CH_3, are reported. These compounds were prepared from reaction of phosphorus trichloride and corresponding amines. Evidence for formation of these molecules, either in solution or in the solid, based on ^1H, ^{31}P NMR, IR, MS and X-ray crystallography has been obtained. $(o\text{-}CH_3C_6H_4NH_3^+)(^-O)P(:O)_2H$ crystallizes from ethanol/chloroform and is triclinic (m.p. 158–160°C) in space group P-1, with unit cell parameters a = 4.6782(13) Å, b = 9.574(3) Å, c = 11.253(4) Å, $\alpha = 107.18(4°)$, $\beta = 101.37(4)°$, $\gamma = 96.99(3)°$ and Z = 2. The crystal structure, solved by direct methods, and refined to $R_1 = 0.0474$ and $wR_2 = 0.0699$ for 2010 observed reflections. The P—O distances are 1.499(3) Å, 1.499(3) Å and 1.565(3) Å. The O—P—O angles are 116.5(2)°, 107.53(18)° and 111.97(18)°. $(p\text{-}CH_3C_6H_4NH_3^+)(^-O)P(:O)_2H$ crystallizes from DMF/ethanol or ethanol and is orthorhombic (m.p. 174–176°C) in space group pca21, with unit cell parameters a = 14.003 Å, b = 8.908 Å, c = 7.451 Å; $\alpha = \beta = \gamma = 90°$ and Z = 4. The crystal structure is solved by direct methods, and refined to R1 = 0.0427 and wR2 = 0.0871 for 5580 observed reflections. The P—O distances are 1.481(2) Å, 1.493(3) Å and 1.540(3) Å. The O—P—O angles are 114.79(14) Å, 112.86(15) Å and 108.07(18)°. The P—O distances and O—P—O angles show that these compounds have two identical P═O and one P—O bonds.

Key Words: Synthesis, Primary ammonium phosphonate, X-ray, NMR.

INTRODUCTION

Some 100,000 phosphorus compounds were known by 1970 and many thousands more have been prepared since then; many derivatives of phosphorus such as phosphates, phosphonates and phosphoracid esters and phosphor amides have been known in the literature. These compounds have been used for a variety of purposes: agricultural chemicals, medicinal compounds, catalysts, flame retardant for fabrics and plastics, plasticising and stabilizing agents in the plastics industry, selective extractants for metal salts from ores, additives for petroleum products and corrosion inhibitors. Organophosphorus compounds are versatile intermediates in organic and inorganic synthesis[1–6]. Phosphorus compounds which have P—H bond are used in the formation of P—C bond in reaction with RCH═CH_2, R = aryl and alkyl[7–10].

Syntheses and reaction of compounds with P(:O)H and PO_4 group have been previously reported[1–2, 11–16] but there is no compound with $(^-O)P(:O)_2H$ group.

As PF_6– has one negative charge. we believe these compounds with PO_3H^- group have also analogous structure and same negative charge. These compounds are synthesized easily and can apply instead of PF_6^- as a counter ion. In this paper we exhibit the first class of compounds with structure R—$C_6H_4NH_3(^-O)P(:O)_2H$. Because of the potential usefulness of compounds **1–4** in further syntheses, we undertook a detailed study of the syntheses and crystallization properties, NMR and IR spectroscopy of these compounds.

EXPERIMENTAL

Caution: Although no poisoning was observed during these studies, organophosphorus compounds have potentially neurotoxic action. They should be handled only with proper safety precautions.

Chemicals were obtained from Merck. Aniline, *o*-toluidine and *m*-toluidine were distilled before use. *p*-Toluidine was purified with standard method[17]. Infrared (4000–400 cm^{-1}) and mass spectra were obtained with FT, Galaxy 5000 Matteson and VG TRIO-2000 GC/MS, respeetively. ^1H and ^{31}P NMR spectra were recorded on a JEOL FX90Q Fourier transform spectrometer equipped with standard probe accessories and reported in ppm. ^1H and ^{31}P NMR spectra were obtained at 89.603 MHz and 36.262 MHz, respectively. ^1H and ^{31}P chemical shifts are recorded relative to TMS and 85% H_3PO_4 (external) and +δ values are downfield from the standard. All NMR spectra were obtained at 25°C. Elemental analyses were carried out by an elemental analyzer.

Preparation of $(C_6H_5NH_3^+)(^-O)P(:O)2H$ (1): Aniline (180 mmol) in THF (40 mL) was added dropwise to a stirred solution of phosphorus trichloride (30 mmol) in THF (40 mL) at 0°C in an ice-water bath. The reaction mixture was stirred for 6 h and then allowed to stand for 48 h at room temperature to ensure complete reaction. After this time anilinium hydrochloride was removed by filtration and then washed with THF (20 mL). The filtrate and washing were distillated in vacuum to give a yellow oil which was washed with carbon tetrachloride and dilute hydrochloric acid for removal of unreacted *o*-toluidine. For further purification, the remaining solid was washed with dilute hydrochloric acid and water until the washings gave no chloride test. Further the solid was dissolved in minimum amount of DMF to give crystals of **(1)**. It was purified by crystallization in ethanol/chloroform and colourless crystals of **(1)** as needles were obtained; yield 3.9 g (75%), m.p. 158–160°C., Analysis: Calcd. for $C_6H_9NO_3P$ (1): C, 41.39; H, 5.21; N, 8.04; Found: C, 41.45; H, 5.25; N, 8.10. IR (KBr) (cm^{-1}): 3178 (m), 2901 (s), 2621 (m), 2367 (s), 1784 (w), 1570 (s), 1499 (vs), 1219 (s), 1205 (s), 1148 (vs), 1092 (s), 1030 (s), 972 (m), 928 (s), 748 (s), 690 (m), 559 (s), 484 (s), 414 (m); MS, a strong parent peak at m/e 94.1, attributable to $C_6H_5NH_3^+$ is seen along with a series of less intense species.

^1H NMR (DMSO-d_6): 6.724 (d, $^1J_{PH}$ = 628 Hz); 7 (multiplet); 8.557 ppm .

^{31}P NMR (DMSO-d_6; AX pattern): δ 3.181 ppm (d, $^1J_{PH}$ = 628 Hz).

Preparation of $(o\text{-}CH_3C_6H_5NH_3^+)(^-O)P(:O)_2H$ (2): To a benzene (25 mL) solution of phosphorus-trichloride (50 mmol) was added slowly with stirring 300 mmol of *m*-toluidine in THF (30 mL) at 0°C. The mixture was left at room temperature for 24 h and the suspension was mixed with water. The organic layers were distilled in vacuum and the obtained solid was washed with carbon tetrachloride and dilute hydrochloric acid. The solid was washed with water and recrystallized from DMF. Repeated recrystallization from ethanol/chloroform mixture gave pure (2); yield 7.05 g (75%), (m.p. 158–160°C), Anaysis: Calcd. for $C_7H_{11}NO_3P$: C, 44.68; H, 5.89; N, 7.44. Found: C, 44.30; H, 5.99; N,7.33. IR (KBr) (cm^{-1}): 3398 (w), 2920 (s), 2671 (m), 2611 (s), 2401 (s), 2361 (m), 2131 (w), 1638 (m), 1560 (m), 1497 (m), 1396 (w), 1217 (m), 1147 (s), 1117 (s), 1035 (vs), 996 (vs), 937 (s), 754 (s), 553 (s), 523 (w), 459 (s), 441 (m). MS, parent and five most intense envelopes, m/e (% relative intensity): 108.1 [100; $CH_3C_6H_4NH_3^+$], 89.0 (33), 77.0 (36), 63.0 (25), 51.0 (34).

^1H NMR (DMSO-d_6): 2.107, 6.8 (multiplet), 7.058 (d, $^1J_{PH}$ = 633 Hz) and 7.666 ppm.

^{31}P NMR (DMSO-d_6; AX pattern): δ 3.363 ppm (d, $^1J_{PH}$ = 633 Hz).

X-ray Structure Analysis of 2: Crystallization of **2** from DMF or ethanol yielded crystals of **2** suitable for X-ray analysis. Cell parameters were determined on a Stoe IPDS diffractometer using graphite monochromated Mo-radiation by full-matrix least squares procedures[18–22]*.

Preparation of (m-$CH_3C_6H_4NH_3^+$)($^-$O)P(:O)$_2$H (3): The method of preparation of **3** is similar to that of **2**; yield 7.33 g (78%), (m.p. 148–150°C). Analysis: Calcd. for $C_7H_{11}NO_3P$: C, 44.68; H, 5.89; N, 7.44; Found: C, 44.60; H, 5.90; N, 7.40. IR (KBr) (cm^{-1}): 2908 (s), 2631 (s), 2403 (m), 2144 (w), 2079 (w), 1683 (w), 1579 (m), 1485 (m), 1207 (w), 1128 (vs), 1008 (vs), 927 (s), 783 (s), 688 (m), 550 (m), 461 (s), 442 (m).

MS is the same as (**2**).

^1H NMR (DMSO-d_6): 2.201; 6.714 (d, $^1J_{PH}$ = 629 Hz); 7.028 (multiplet), 8.072 ppm.

^{31}P NMR (DMSO-d_6; AX pattern): δ 2.827 (d, $^1J_{PH}$ = 622 Hz).

Preparation of (p-$CH_3C_6H_4NH_3^+$)($^-$O)P(:O)$_2$H (4): Preparation of (**4**) is the same as **1**; yield 4.79 g (85%), (m.p. 174–176°C). Analysis: Calcd, for $C_7H_{11}NO_3P$: C, 44.69; H, 5.89; N, 7.44; Found: C, 44.72; H 5.82; N, 7.45. IR (KBr) (cm^{-1}): 2866 (s), 2619 (s), 2394 (s), 2141 (m); 1818 (w, sh), 1645 (m), 1554 (s), 1516 (s), 1224 (s), 1215 (s), 1140 (vs), 997 (vs), 966 (s), 814 (s), 642 (w, sh), 567 (s), 497 (s), 437 (s).

MS is the same as (**2**).

^1H NMR (DMSO-d_6): 2.191; 6.702 (d, $^1J_{PH}$ = 626 Hz); 6.85 (multiplet), 7.63 ppm.

^{31}P NMR (DMSO-d_6; AX pattern): δ 2.392 (d, $^1J_{PH}$ = 617 Hz).

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RESULTS AND DISCUSSIONS

In the crystal structure of (2) the P—O_1 and P—O_2 bond lengths are equivalent (1.499 Å) which indicates that the oxygen atoms are essentially equivalent. These two P—O bond distances, found in this study, are virtually equivalent and are the same with expected values for P=O bond lengths. The other, P—O_3 bond length (1.565 Å) is near to the single bond between phosphorus and oxygen (Table-1). Cell parameters and crystal structure of (2) are shown in Tables 2–4 and Fig. 1, respectively. The crystal structure parameters of (4) are shown in Tables 2, 4 and 6. The PO_1 and PO_2 distances of (4) are also equivalent (1.481 and 1.493 Å) and these are close to P=O bond distances that are found in other molecules which were previously reported[23–33]. The P—O_3 bond distance (1.540 Å) is equivalent with P—O single bond length (Table-2). The X-ray structure of (4) is shown in Fig. 2.

TABLE-1
PHOSPHORUS-OXYGEN BOND DISTANCES (Å)

$D_{Calc.}$, single, 1.76; double, 1.57; triple, 1.43

Compound	$D_{Observed}$	Method	Ref.
POF_3, POF_2Cl, $POFCl_2$, $POCl_3$	1.55 ± 0.03	E.D.	23
$[(—O—)_3PO']_4$	PO′ 1.39 ± 0.02	E.D.	24
	PO 1.62 ± 0.02		
$[(—O—)_3P]_4$	PO 1.62 ± 0.02	X-ray cryst.	24
$[(—O—)_3P]_2PdCl_2$	1.584	X-ray cryst.	25
$[(—O—)_3P]_2PtCl_2$	1.575	X-ray cryst.	26
$[(—O—)_3P]_2PtBr_2$	1.586	X-ray cryst.	27
$NH_4H_2PO_4$	1.51 ± 0.11	X-ray cryst.	28
KH_2PO_4	1.56	X-ray cryst.	29
Ag_3PO_4	1.61 ± 0.03	X-ray cryst.	30
Phosphates	1.55	X-ray cryst.	31
$(C_6H_5)_2P(=O)OH$	P=O 1.486(6)	X-ray cryst.	32
	P—OH 1.526(6)	X-ray cryst.	32
$Na[PO_3.NH_3]$	1.522(6)	X-ray cryst.	16
$(Me_3C)P(O)OH$	1.520	X-ray cryst.	33
	1.521	X-ray cryst.	33
$(o\text{-}CH_3C_6H_4NH_3^+)(^-O)P(:O)_2H$	2P=O 1.499	X-ray cryst.	*
	P—O^- 1.565	X-ray cryst.	*
$(p\text{-}CH_3C_6H_4NH_3^+)(^-O)P(:O)_2H$	2P=O 1.481 and 1.493	X-ray cryst.	*
	P—O^- 1.540?	X-ray cryst.	*

E.D.	electron-diffraction investigation of vapour.
‘X-ray cryst.	X-ray diffraction investigation of the crystal.

TABLE-2
CRYSTAL DATA AND STRUCTURE REFINEMENT

	$(o\text{-}CH_3C_6H_4NH_3^+)(^-O)P(:O)_2H$ **(2)**	$(p\text{-}CH_3C_6H_4NH_3^+)(^-O)P(:O)_2$ **(4)**
Empirical formula	$C_7H_{11}NO_3P$	$C_7H_{11}NO_3P$
Fomula weight	188.16	188.16
Temperature	293 (2) K	293 (2) K
Wavelength	0.7173 A	0.71073 A
Crystal system, space group	Triclinic, P-1	Orthorhombic, P C a 21
Unit cell dimensions (deg.)	a = 4.6782(13) A, α = 107.18(4) deg, b = 9.574(3) A, β = 101.37(4) deg c = 11.253(4) A, γ = 96.99(3) deg	a = 14.003 A, α = 90 deg b = 8.908 A, β = 90 deg c = 7.451 A, γ = 90 deg
Volume	463.3(2) A^3	929.4 A^3
Z, calculated density	2, 1.349 mg/m^3	4, 1.345 mg/m^3
Absorption coefficient	0.217 mm^{-1}	0.216 mm^{-1}
F (000)	198	396
2θ range for data collection	4.54–48.16 deg	4.58 to 48.56 deg.
Reflections collected/unique	2010/1306 [R (int) = 0.0362]	5580/1465 [R(int) = 0.1187]
Completeness to 2θ = 48.16	88.8%	97.6%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F2
Data/restraints/parameters	1306/0/122	1465/1/125
Goodness-of-fit on F2	0.978	0.814
Final R indices [I > 2σ (I)]	R_1 = 0.0474, wR_2 = 0.1274	R_1= 0.0427, wR_2= 0.0790
R indices (all data)	R_1 = 0.0699, wR_2 = 0.1350	R_1= 0.0871, wR_2= 0.0887
Largest diff. peak and hole	0.317 and –0.199 e . A^{-3}	0.259 and –0.285 e/A^{-3}

TABLE-3
ATOMIC COORDINATES (× 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($A^2 \times 10^3$) FOR (2)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(rq)
P(1)	8433(1)	8771(1)	7414(2)	8(1)
C(1)	9133(4)	4808(1)	5254(8)	49(2)
C(3)	8983(3)	2651(5)	3425(8)	28(1)
C(4)	8686(3)	3491(6)	1979(7)	35(1)
C(6)	8606(3)	5017(6)	2207(10)	47(2)
C(2)	9208(4)	3304(6)	5048(7)	39(2)
C(7)	8824(4)	5676(7)	3849(9)	51(2)
N(1)	9074(3)	1015(5)	3246(6)	28(1)
O(1)	8696(2)	8965(5)	9442(2)	40(1)
O(2)	7492(2)	9482(4)	6968(4)	41(1)
O(3)	9276(2)	9278(4)	6331(4)	38(1)
C(5)	8488(4)	2782(7)	188(6)	45(2)

TABLE-4

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($A^2 \times 10^3$) FOR (4)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(rq)
C(1)	2494(13)	9122(6)	7264(4)	94(2)
C(2)	1018 (9)	8182(4)	5899(4)	55(1)
C(3)	–550 (2)	6837(9)	5649(8)	52(2)
C(4)	–1777(17)	5909(8)	4408(7)	44(2)
C(5)	–1551 (7)	6454(3)	3401(3)	36(1)
C(6)	2(18)	7862(8)	3617(7)	46(2)
C(7)	1166(17)	8756(8)	4871(7)	47(2)
C(3′)	–1650 (2)	7249(9)	5595(8)	49(2)
C(4′)	–3053(19)	6429(8)	4336(7)	42(2)
C(6′)	1190(18)	7316(8)	3697(7)	42(2)
C(7′)	2599(18)	8127(7)	4965(7)	44(2)
O(1)	1253 (5)	3761(2)	1457(2)	45(1)
O(2)	3701 (5)	2934(3)	–354(2)	50(1)
O(3)	–1651 (6)	2043(4)	–726(3)	92(1)
N(1)	–2879 (8)	5515(4)	2082(3)	43(1)
P(1)	1343 (2)	2563(1)	285(1)	42(1)

TABLE 5

BOND LENGTHS [Å] AND ANGLES [DEG] FOR (2)

P(1)–O(3)	1.499(3)	O(3)–P(1)–O(2)	116.5(2)
P(1)–O(2)	1.499(3)	O(3)–P(1)–O(1)	107.53(18)
P(1)–O(1)	1.565(3)	O(2)–P(1)–O(1)	111.97(18)
C(1)–C(2)	1.353(7)	C(2)–C(1)–C(7)	119.8(6)
C(1)–C(7)	1.371(8)	C(4)–C(3)–C(2)	121.8(4)
C(3)–C(4)	1.376(7)	C(4)–C(3)–N(1)	119.6(5)
C(3)–C(2)	1.378(7)	C(2)–C(3)–N(1)	118.6(5)
C(3)–N(1)	1.469(6)	C(6)–C(4)–C(3)	117.7(5)
C(4)–C(6)	1.375(7)	C(6)–C(4)–C(5)	120.7(6)
C(4)–C(5)	1.502(7)	C(3)–C(4)–C(5)	121.5(5)
C(6)–C(7)	1.391(9)	C(4)–C(6)–C(7)	120.5(6)
		C(1)–C(2)–C(3)	120.0(5)
		C(1)–C(7)–C(6)	120.2(6)

TABLE-6
BOND LENGTHS [Å] AND ANGLES [deg] FOR (4)

P(1)–O(1)	1.481(2)	O(1)–P(1)–O(2)	114.79(14)
P(1)–O(2)	1.493(3)	O(1)–P(1)–O(3)	112.86(15)
P(1)–O(3)	1.540(3)	O(2)–P(1)–O(3)	108.07(18)
C(1)–C(2)	1.498(6)	C(3)–C(2)–C(7′)	109.05(5)
C(2)–C(3)	1.335(9)	C(3)–C(2)–C(3′)	29.3 (4)
C(2)–C(7′)	1.373(8)	C(7′)–C(2) –C(3′)	119.4 (3)
C(2)–C(3′)	1.385(10)	C(3)–C(2)–C(7)	118.9 (5)
C(2)–C(7)	1.425(8)	C(7′)–C(2) –C(7)	40.3 (4)
C(3)–C(4)	1.376(10)	C(3′)–C(2)–C(7)	107.5 (5)
C(4)–C(5)	1.397(8)	C(3)–C(2)–C(1)	119.4 (5)
C(5)–C(6′)	1.359(8)	C(7′)–C(2) –C(1)	120.4 (5)
C(5)–C(6)	1.378(8)	C(3′)–C(2) –C(1)	119.9 (5)
C(5)–C(4′)	1.380(8)	C(7)–C(2)–C(1)	121.3 (4)
C(5)–N(1)	1.452(4)	C(2)–C(3)–C(4)	121.3 (7)
C(6)–C(7)	1.375(10)	C(3)–C(4)–C(5)	118.8 (6)
C(3′)–C(4′)	1.380(11)	C(6′)–C(5)–C(6)	34.8 (4)
C(6′)–C(7′)	1.387(10)	C(6′)–C(5) –C(4′)	121.1 (5)
		C(6)–C(5)–C(4′)	111.7 (5)
		C(6′)–C(5)–C(4)	108.5 (5)
		C(6)–C(5)–C(4)	121.7 (5)
		C(4′)–C(5)–C(4)	34.7 (3)
		C(6′)–C(5)–N(1)	119.2 (4)
		C(6)–C(5)–N(1)	118.2 (4)
		C(4′)–C(5)–N(1)	119.6 (4)
		C(4)–C(5)–N(1)	120.1 (4)
		C(7)–C(6)–C(5)	117.6 (6)
		C(6)–C(7)–C(2)	120.8 (6)
		C(4′)–C(3′)–C(2)	120.7 (7)
		C(5)–C(4′)–C(3′)	118.5 (7)
		C(5′)–C(6)–C(7′)	120.1 (6)
		C(2)–C(7′)–C(6′)	119.4 (7)

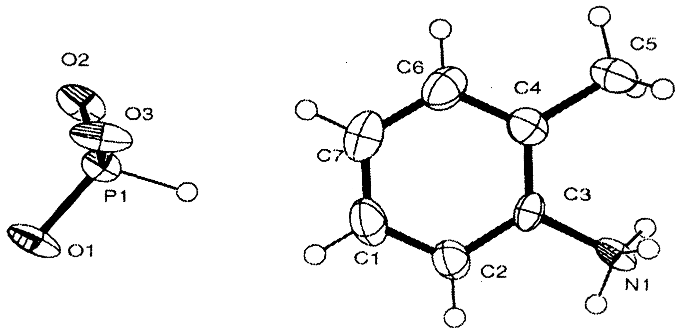

Fig. 1. Crystal structure of (o-$CH_3C_6H_4NH_3^+$)(^-O)P(:O)$_2$H (2) (Ortep diagram)

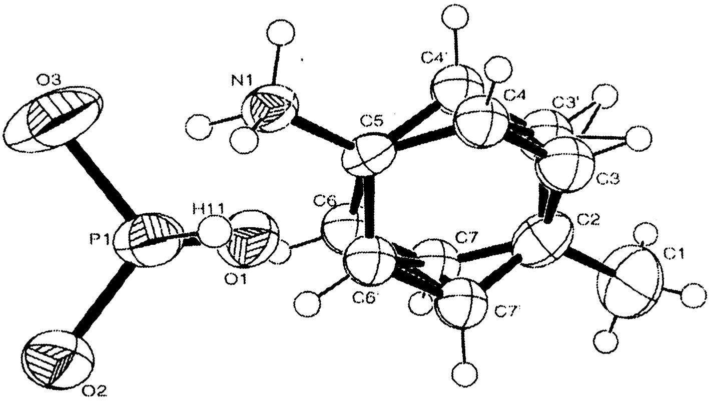

Fig. 2. Crystal structure of (p-$CH_3C_6H_4NH_3^+$)(^-O)P(:O)$_2$H (4) (Ortep diagram)

The MS shows peak of (*R*—$CH_3C_6H_4NH_3^+$) or ($C_6H_5NH_3^+$) with 100% intensity. IR spectra of these molecules in region 1350–1100 cm^{-1} show the vibrational frequencies of PO bonds (ν_{PO}) and have several peaks in this region which shows these compounds have different PO bonds and these are consistent with X-ray structures[34–41]. The ^{31}P NMR data of all of these compounds confirm that (*R*—$C_6H_4NH_3^+$)(^-O)P(:O)$_2$H in solution is phosphonate oxide (1), (2), (3), (4) and not the phosphonate with P-OH group. The chemical shift of **(1)** to **(4)** [2.392 to 3.363 ppm] also occurs in phosphine oxide region. All ^{31}P NMR spectra show splitting with hydrogen and the large amount of coupling constant $^1J_{PH}$ (617-633 Hz) confirm that the hydrogen directly is bonded to phosphorus atom. The ^1H NMR sectra are also consistent with these results[12, 42, 43].

Thus, it is clear from cell parameter of crystal structure of (**2** and **4**) (Tables 2–6) that the two PO bond distances are equivalent (1.499 Å in **2** and about 1.487 Å in **4**) and are shorter than other PO bonds (1.565 Å in **2** and 1.540 Å in **4**). This result tends to favour the expected model in Fig. 3. In this model there is a negative charge on one oxygen atom that has longer bond distance with phosphorus atom.

Although there are six bonds for phosphorus atom, but three of these bonds are with oxygen (two double and one single bond) which decrease electron density on phosphorus atom. The oxygen with longer distance (Fig. 3) possesses the electron density which leads to deshielding of hydrogen atom with higher frequency in δ ^{1}H of *ca.* 6.7 ppm for these compounds. These qualitative arguments can also be extended to J values and ^{31}P chemical shifts in these compounds (Table-7).

TABLE-7

J_{PH} VALUES FOR PREPARED COMPOUNDS

Compound		$J_{P\text{-}H}$ (Hz)	δ (^{31}P) ppm	δ (^{1}H) ppm
$(C_6H_5NH_3^+)(^-O)P(:O)_2H$	(1)	628	3.181	6.720
$(o\text{-}CH_3C_6H_5NH_3^+)(^-O)P(:O)_2H$	(2)	633	3.363	6.800
$(m\text{-}CH_3C_6H_5NH_3^+)(^-O)P(:O)_2H$	(3)	622	2.827	6.710
$(p\text{-}CH_3C_6H_5NH_3^+)(^-O)P(:O)_2H$	(4)	617	2.392	6.700
$(C_6H_5NH)_2P(O)_2H$	[Ref. 12]	600	1.100	7.340

As one can see there is apparant increase in δ and j values for phosphorus atom (1)–(4) in comparing with $J_{P\text{-}H}$ = 600 Hz in simillar compound[12, 42, 43]. This is probably due to relation between $^{1}J_{PH}$ and δ ^{31}P. As electron density decreases on phosphorus atom there is an increase on δ ^{31}P, $^{1}J_{PH}$ and $\delta_{H(P\text{-}H)}$ values, where all are consistent with Fig. 3.

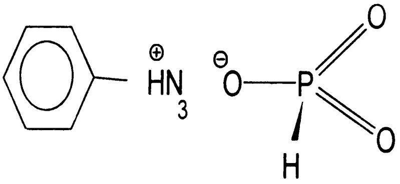

Fig. 3. Expected model for **$(C_6H_4NH_3^+)(^-O)P(:O)_2H$ (2)**

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