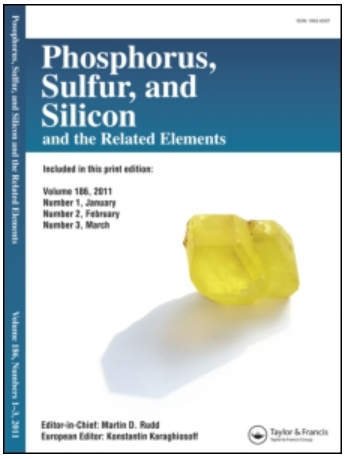

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SYMMETRIC AND ASYMMETRIC DIISOPROPOXYPHOSPHORYL GUANIDINES

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Phosphorylation of guanidines and alkanediyldiguanidines by a two-phase reaction gave asymmetric (I) and symmetric (III) organophosphorus compounds containing 1-phosphoryl-3-imino group. Structural analyses carried out by IR and NMR coupling/decoupling spectroscopy. Temperature dependence studies showed the presence of intramoleuclar hydrogen bonding of the developed system, the influence of steric effect on the tautomerism of the system was also investigated.

Keywords: Phosphorylation; diisopropyl phosphite; symmetric phosphorylguanidines; organophosphorus containing 1-phosphoryl-3-carbonyl group

INTRODUCTION

Bidentate compounds containing a 1-phosphoryl-3-carbonyl group are known to form colorful complexes with various metal ions[1]. They are powerful extractants for trivalent lanthanides and actinides as well as alkali metal cations[2,3]. An alternation of the molecular structure might improve the extractant properties of these compounds, such as the complexing capacity and the ion selectivity. We have reported the syntheses and preliminary complexation studies of the compounds derivatives of guanidine and isothiourea[4–6]. Now we describe the synthesis and structure analysis of the asymmetric (I) and symmetric (III) phosphorylguanidines.

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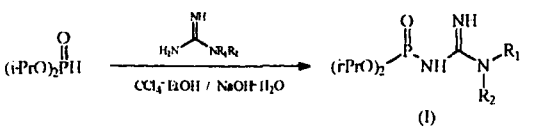
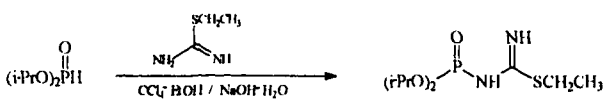
RESULTS AND DISCUSSION

Reaction of diisopropyl phosphite with guanidines and S-ethyl isothiourea[4] in CCl_4/H_2O gave the desired products, (I) and (II) respectively, in good yield. The reaction of diamine (ethylenediamine, 1,4-butanediamine...etc.) with phosphoryl isothiourea (II) at 90°C gave the symmetric diphosphorylguanidine (III) in low yield. This diphosphorylated compound (III) could also be obtained in good yield by a direct phosphorylation reaction of alkanediyldiguanidine (IV) with diisopropyl phosphite. The diguanidine (IV) was prepared by reacting diamine with S-ethyl isothiourea[7].

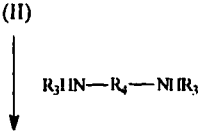


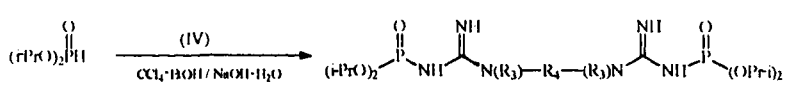
(I)

a, R_1, R_2= H; b, R_1= H; R_2=CH_3; c, R_1= R_2= CH_3



(II)

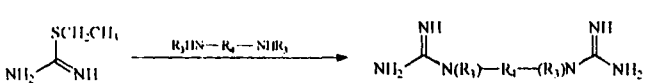




(III)

a, R_3=H; R_4= -$(CH_2)_2$-; b, R_3=H; R_4= -$(CH_2)_4$-

c, R_3=CH_3; R_4= -$(CH_2)_2$-



(IV)

Compounds (I) and (III) showed characteristic IR absorption peaks at around 3400 (N-H), 1620 (C=N), 1200 (P=O) and 1000 (P-O-C) cm^{-1}. The absorption of group P=O at lower than the normal wave number (1250–1300 cm^{-1})[8] suggests a possible hydrogen bonding involving oxygen atom which will weaken the bond between phosphorus and oxygen atoms, consequently shifts this peak to a lower wave number. No absorption peak of P=N at around 1350 cm^{-1} was observed[8]. The ^{1}H-NMR spectra showed the characteristic doublet at around δ=1,35 ppm for the methyl group and a symmetric multiplet at around δ=4.5 ppm for the hydrogen atom of -CH-O group suggesting the presence of the coupling between phosphorus and hydrogen nuclei[9]. All the hydrogen atoms connected to amino nitrogen appeared as a broad peak at around δ=6.0 ppm. ^{31}P NMR decoupled spectra showed a single peak at around 5.5 ppm for the monophosphoryated guanidine (I) and at around 8.5 ppm for the diphosphorylated compounds (III). A completely proton coupled ^{31}P NMR spectrum of compound (Ia) showed a quartet at 6.0 ppm suggesting that the nucleus P is coupled with at least 3 other protons (Fig. 1(a)). Irradiation at the chemical shift of the proton of -CH-O- at δ=4.49 ppm the ^{31}P NMR spectrum changed to a doublet (Fig. 1(b)) confirming the coupling between nuclei P and H of -CH-O- group. Irradiation at chemical shift of the proton of P-NH- group at δ=6.5 ppm the ^{31}P NMR spectrum changed to a triplet (Fig. 1(c)) confirming the coupling between nuclei P and H of P-NH- group. No change of ^{31}P NMR spectrum was observed while irradiation was carried out at the chemical shift of the proton of =NH group at δ=6.18 ppm (Fig 1(d)). The same NMR decoupling studies carried out on compound (Ic) showed that phosphorus nucleus only couples with hydrogen of O-CH group (Fig. 2).

Theoretically there are three possible tautomers for compound (I): A, B and C. The absence of P=N absorption in IR spectra eliminates the possibility of tautomer C. The ^{31}P, ^{1}H NMR coupling and decoupling studies of compound (I) suggest that the tautomer A predominates at ground state for phosphorylguanidine (Ia) and its mono alkylated product (Ib) while for dialkylated phosphorylguanidine (Ic) tautomer B becomes more important.

Temperature dependence ^{1}H NMR studies of compound (Ia) showed that when temperature was reduced the peak from amino hydrogens broadened and disappeared at -30 °C. Further cooling to –60 °C the spectrum modi-

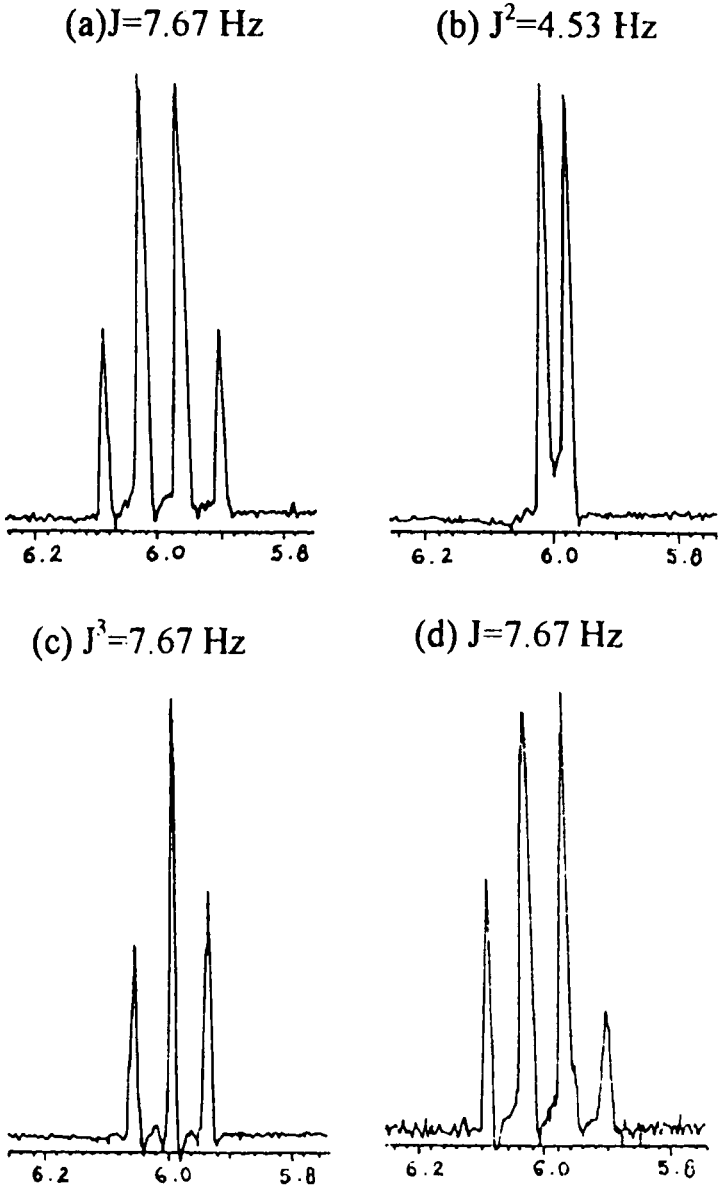


FIGURE 1 ^{31}P NMR decoupled/coupled spectra of diisopropoxyphosphoryl guanidine (Ia) (a) completely coupled; (b) decoupled with -CHO- at 4.49 ppm; (c) decoupled with P-NH at 6.5 ppm; (d) decoupled with =NH at 6.18 ppm

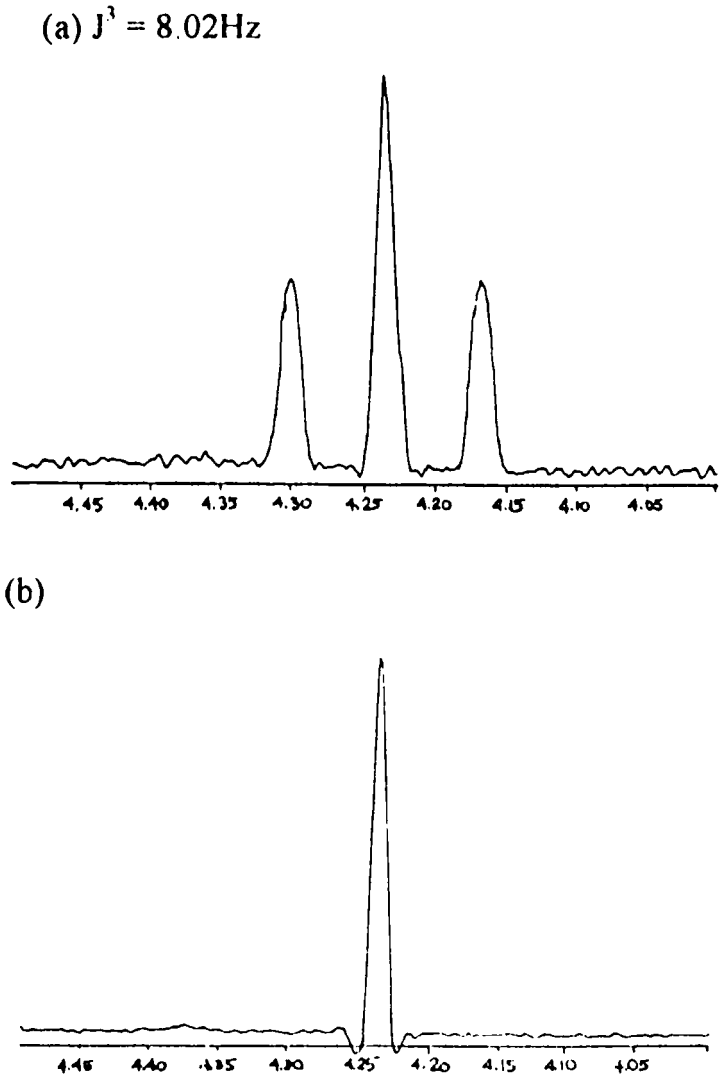
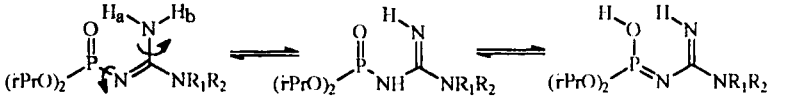


FIGURE 2 ^{31}P NMR decoupled/coupled spectra of N'N'-dimethyl diisopropoxyphosphoryguanidine (Ic), (a) completely coupled; (b) decoupled with -CHO- at 4.48 ppm

fied to two new peaks at 1:1 intensity at δ 5.75 and 6.90 ppm (Fig. 3(a)). At room temperature the rotations between C-N bonds and the equilibrium between tautomers A and B are very rapid that no difference between



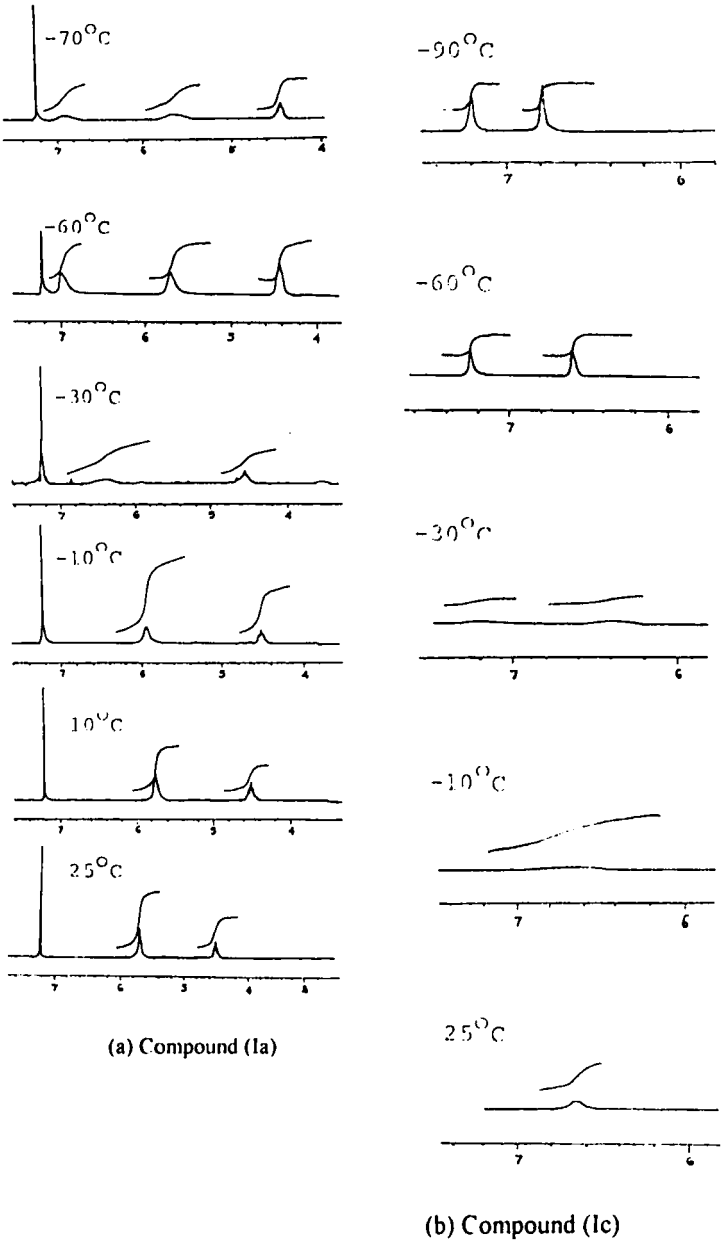
B A C

amino protons could be observed; at lower temperature (-60 °C) the bond rotation slows down and the equilibrium of tautomerisum shifts to a more favorable tautomer B giving two amino groups in different neighborhood. One of the proton (H_a or H_b) is able to form intramolecular hydrogen bonding, however, the rotation between C-N bond is still very rapid at this temperature that no difference between these two hydrogens was observed. Compound (Ic) shows a similar behavior on temperature dependence ^1H NMR studies (Fig. 3(b)), however, the introduction of two methyl groups on the same nitrogen atom makes the dimethylamino group so bulky that it would stay preferably on the less hindered side forcing the unsubstituted amino group to stay on the skeleton of six membered ring which favors a possible intramolecular hydrogen bonding. Once the temperature is low enough the rotation between C-NH_2 slows down to an extent that different boned protons ($H_a$and H_b) were observed. Symmetric diphosphorylated guanidine (III) demonstrated a similar behavior.

Both mono- and di- phosphorylated guanidines (I) and (III) showed the molecular ion plus one peak in their mass spectra. These compounds demonstrated McLafferty rearrangement to give characteristic fragments and a common peak at 123 with very high intensity. The diphosphorylated guanidine (III) also presented a characteristic α-cleavage of aliphatic amine to give a resonance-stabilized iminium ion. Figure 4 shows the basic fragmentation of these compounds.

EXPERIMENTAL

The NMR spectra (^1H, ^{13}C and ^{31}P) were recorded on a Bruker AC300 spectrometer. All chemical shifts are reported with respect to TMS or



(a) Compound (Ia)

(b) Compound (Ic)

FIGURE 3 Temperature dependence ^1H NMR spectra of compounds (Ia) and (Ic)

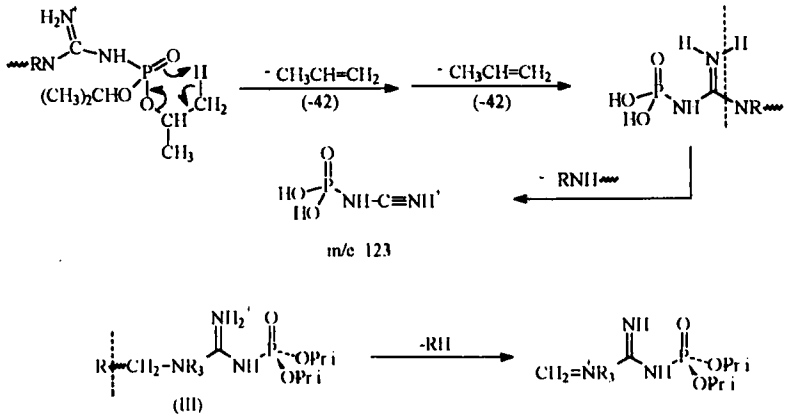


FIGURE 4 Fragmentation of mono and diphosphorated guanidine (I) and (III)

H_3PO_4. IR spectra were obtained on a Perkin-Elmer Model 1710 spectrometer. Mass spectra were taken on a Varian MAT 8500 (70 eV) spectrometer. Melting points were taken on a Fisher-Johns melting point apparatus without correction.

Phosphorylation of alkylated guanidine

General Procedure

Alkylated guanidine hydrochloride (0.01 mol) and sodium hydroxide (0.02 mol) were dissolved in a mixture of 10 ml of water and 2 ml of ethanol. This solution was cooled to 0 °C and a solution of diisopropylphosphite (0.01 mol) in 10 ml of carbon tetrachloride was added dropwise at this temperature. The mixture was stirred at 50 °C for 4 hours. After the reaction, 10 ml each of water and chloroform (1:1) were added. The organic layer was separated and the aqueous solution was extracted three times with chloroform (5 ml portions). The organic layers were combined, washed once with 5 ml of water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuum to give the crude product.

Diisopropoxyphosphorylguanidine (Ia) and Diisopropoxyphosphoryl S-ethylisothiourea (II)[5]

These compounds were prepared by following the procedure of reference 5.

N′-methyl diisopropoxyphosphorylguanidine (Ib)

Recrystalized from cyclohexane, m.p. 80–81 °C. IR (KBr plate): 3345; 3273; 3195(NH); 1649(C=N), 1210(P=O); 1001(P-O). ^{1}H NMR($CDCl_3$)(ppm): 1.27(d, J=6.00, 12H, CH_3); 2.73(d, J=4.40, 3H, NCH_3); 4.32–4.48 (m, 2H, CH); 6.18(broad singlet, 2H, NH_2); 6.50(s, 1H, NH). ^{13}C NMR(DMSO-D_6): 23.71(d, J=8.29, CH_3); 27.30 (s, NCH_3); 68.48(d, J=5.50, CH); 156.74(d, J=2.03, C=N). ^{31}P NMR: 5.41. Mass Spec. 238 (M^++1), 154; 123. Anal. Calcd for $C_8H_{20}O_3N_3P$: C, 40.51; H, 8.44; O, 20.25. Found: C, 40.53; H, 8.42; O, 20.19.

N′,N′-dimethyl diisopropoxyphosphorylguanidine (Ic)

The liquid crude product solidified in freezer, m.p. 38 °C. IR(nijol): 3418; 3338; 3243(NH); 1638(C=N); 1195(P=O); 997(P-O). ^{1}H NMR($CDCl_3$)(ppm): 1.24(d, J=6.41, 12H, CH_3); 2.93(s, 6H, $N(CH_3)_2$); 4.34–4.49(m, 2H, CH); 5.98(broad singlet, 2H, NH_2); ^{13}C NMR: 23.77(d, J=4.82, CH_3); 23.80 (d, J=4.90, CH_3); 36.86, 36.89($(NCH_3)_2$): 69.59(d, J=5.58,CH); 157.88(d, J-9.88, C=N). ^{31}P NMR: 5.61. MS (m/e): 252 (M^++1); 168; 123. Anal. Calcd for $C_9H_{22}O_3N_3P$: C, 43.02; H, 8.76; O, 19.12. Found: C, 43.00; H, 8.80; O, 19.00.

Synthesis of symmetric phosphorylguanidine

General Procedure

Compound (II) (0.012 mol) was dissolved in 30 ml of toluene and 0.006 mol of appropriate diamine was added. The solution was heated at 90 °C for many hours until no more mercaptan was liberated. The reaction was then worked up to give the crude product.

N_1, N_1′-Ethanediyl-N_2,N_2′-bis(diisopropoxyphosphoryl)diguanidine (IIIa)

Ethylenediamine was used as starting material, the reaction time was 48 hours. Some white crystal was isolated from acetone solution, m.p.

165–7 °C, 10% yield. IR (KBr plate): 3430, 3330, 3201, 3000(NH); 1600(C=NH); 1267(P=O); 991(POC). ^{1}H NMR ($CDCl_3$)(ppm): 1.27(d, J=6.00, CH_3, 24H); 3.27(broad singlet, NCH_2, 4H); 4.46–4.58(oct, J=6.3, CHO, 4H); 6.20(broad singlet, NH, 4H); 7.10(s, NH, 2H); ^{13}C NMR: 23.84, 23.80, 23.78 (CH_3); 41.20 (NCH_2); 70.22 (d, J=6.1, CHO); 158.31, 158.21 (C=N); ^{31}P NMR: 8.6. MS(m/e): 473(M^++1); 237; 123. Anal. Calcd for $C_{16}H_{38}O_6N_6P_2$: C, 40.68; H, 8.05; O, 20.33. Found: : O, 20.33. Found: C, 40.51; H, 7.95; O, 20.38.

N_1, N_1'-Butanediyl-N_2,N_2'-bis(diisopropoxyphosphoryl)diguanidine (IIIb)

1,4-Buatnediamine was used as starting material. The reaction time was 48 hours. The crude product was an oil which gave white crystal on cooling, m.p. 137–9 °C, 12% yield. IR (KBr plate): 3450, 3346, 3276, 3122(NH); 1631(C=NH); 1576(NH); 1253(P=O); 990(POC). ^{1}H NMR ($CDCl_3$) (ppm): 1.36(d, J=6.3Hz, CH_3, 24 H); 1.59(broad singlet, CH_2, 4H); 3.3(broad singlet. NCH_2. 4H); 4.57–4.65(d,hept, J_{HH}=6.3, J_{PH}=7.5, CHO, 4H); δ=6.3(s, NH, 4H); 6.6(s, NH, 2H). ^{13}C NMR: 23.80, 23.73(CH_3); 26.49 (CH_2); 40.00 (NCH_2); 70.07 (d, J=6.00, CHO); 157.84, 157.94 (C=N); ^{31}P NMR: 8.99. MS (m/e): 501(M^++1); 237; 123. Anal. Calcd for $C_{18}H_{42}O_6N_6P_2$: C, 43.20; H, 8.40; O, 19.20. Found: C, 43.30; H, 8.35; O, 19.07.

N_1, N_1'-dimethyl-N_1, N_1'-ethanediyl-N_2,N_2'-bis (diisopropoxyphosphoryl) diguanidine (IIIc)

N,N′-dimethyl ethylenediamine was used as starting material, the reaction time was 48 hours. Some white crystal was isolated without purification, m.p. 125–6 °C, 24% yield. IR (KBr plate): 3210(NH); 1600(C=NH); 1207(P=O); 987(POC). ^{1}H NMR($CDCl_3$) (ppm): 1.29 (d, J=6.00, CH_3, 24H); 3.1 (s, NCH_3, 6H); 3.6 (s, NCH_2, 4H); 4.47–4.58 (m, CHO, 4H), 8.60 (broad singlet, NH, 4H). ^{13}C NMR: 23.84, 23.78, 23.70(CH_3); 32.82(NCH_3); 48.09(NCH_2); 69.66(d, J=6.00, CHO); 158.36(C=N); ^{31}P NMR($CDCl_3$): 8.55. MS (m/e): 501 (M^++1); 251; 123. Anal. Calcd for $C_{18}H_{42}O_6N_6P_2$: C, 43.20; H, 8.40; O, 19.20. Found: C, 43.40; H, 8.66; O, 18.89.

Acknowledgements

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