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New Phosphoric Triamides: Chlorine Substituents Effects and Polymorphism

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ABSTRACT: *New phosphoric triamides* **1**−**10** *were synthesized by the reaction of N-2,4-dichlorobenzoyl phosphoramidic dichloride with various cyclic aliphatic amines, and the products were characterized by* ^{1}H, ^{13}C, ^{31}P *NMR, and IR spectroscopy and elemental analysis. Surprisingly, the* ^{1}H *NMR spectra of compounds* **1**−**7** *demonstrate long-range* $^{4}J(H,H)$ *coupling constant from 1.5 to 1.9 Hz. Comparison of the NMR and IR spectra of N-benzoyl, N-4-chlorobenzoyl, and N-2,4-dichlorobenzoyl phosphoric triamide analogues indicates that N-2,4-dichlorobenzoyl derivatives have the most upfield* $\delta(^{31}P)$ *and the highest* $\nu(C{=}O)$ *values. The crystal structures of* **3**, **4**, **6**, **6a**, *and* **10** *have been determined by X-ray crystallography. Interestingly, the structures of* **6** *and* **6a** *are polymorphic. All structures form dimers through strong, intermolecular* —P=O···H—N— *hydrogen bonds. The dimers connect to each other via weak* C—H···Cl *and* C—H···OH— *bonds to produce two-dimensional polymeric chains for* **4** *and three-dimensional networks for others. Among new synthesized N-2,4-dichlorobenzoyl phosphoric triamides, one indicated polymorphism. All structures were characterized by* ^{1}H, ^{13}C, ^{31}P *NMR, and infrared spectroscopy and elemental analysis.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:168–180, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20592

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INTRODUCTION

The increasing interests in research on phosphoramidates chemistry in the present years are due to the valuable applications of these derivatives as prodrugs [1–3], insecticides and pesticides [4–7], efficient ligands in coordination chemistry [8–11], theoretical chemistry [12,13], synthesis [14–17], and structural study [18–22]. So far, the substituent effects on the structural parameters have been discussed to some extent [23–25]. The crystal structures of several phosphoramidates have already been determined by X-ray crystallography [18–29]. Formation of polymorphs is important not only because of their structural differences but also because of their various therapeutical properties [30]. In recent years, polymorphism has found important applications in the areas of pigments, explosives, electronics, food, agrochemical, and, above all, pharmaceutical industry in which regulatory controls necessitate the close examination of all products under development for their solid-state behavior [31]. Barendt et al. [32] reported two polymorphs of diazaphosphorus compound $C_6H_5P(O)[NHC_6H_4NH]$.

Herein, following on our previous studies, we represent the synthesis, spectroscopic, and structural investigations of 10 new *N*-2,4-dichorobenzoyl phosphoric triamides. Also, we were surprised to obtain two polymorphs of compound $2,4\text{-}Cl_2C_6H_3C(O)NHP(O)(NC_4H_8O)_2$. In addition, the spectroscopic results of these compounds have been compared with those of their *N*-benzoyl and *N*-4-chlorobenzoyl phosphoric triamide analogues.

EXPERIMENTAL

X-ray Measurements

X-ray data of compounds **3, 4, 6,** and **10** were collected by using a Bruker SMART 1000 CCD [33a] and of **6a** by using a Bruker APEX II CCD area detector [33b] single-crystal diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were refined with SHELXL-97 [33–35] by full-matrix least-squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program for these structures [35a,b].

Spectroscopic Measurements

^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Avance DRS 500 spectrometer (Bruker Karlosuhe, Germany). ^{1}H and ^{13}C chemical shifts were determined relative to internal Me_4Si and ^{31}P chemical shifts were determined relative to 85% H_3PO_4 as external standards, respectively. The strong field acquisition of ^{1}H, ^{13}C, and ^{31}P NMR spectra was 500.13, 125.77, and 202.46 MHz, respectively. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer (Shimadzu, Kyoto, Japan). Elemental analysis was performed on a CHN-O-RAPID apparatus (Heraeus, Hanau, Germany). Melting points were determined on an Electrothermal instrument (Electrthermal, Essex, UK).

Synthesis

*N-2,4-Dichlorobenzoyl Phosphoramidic Dichloride (**1**).* A 1:1 molar ratio of phosphorus pentachloride and 2,4-dichlorobenzamide was refluxed in CCl_4 for 8 h and then the resulting solution was cooled to room temperature. Formic acid was syringed dropwise into the stirring solution for 20 min and stirred for 6 h to yield a white precipitate that was filtered and dried in vacuum.

Yield: 71%, m.p. = 120.4°C. Anal. Calcd. for $C_7H_4Cl_4NO_2P$ (%): C, 27.40; H, 1.31; N, 4.56. Found: C, 27.39; H, 1.31; N, 4.55. IR (KBr, cm^{-1}): ν_{max} = 3100 (s), 2850 (w), 1707 (vs, C=O), 1582 (s), 1428 (vs), 1403(s), 1276 (s), 1249 (s), 1227 (vs, P=O), 1142 (w), 1102 (vs), 1043 (m), 896 (s), 866 (w), 832 (m), 781 (m), 756 (m), 678 (m), 586 (m), 516 (m). ^{31}P NMR (202.46 MHz; $CDCl_3$; 85% H_3PO_4): δ 5.99 (m). ^{1}H NMR (500.13 MHz; $CDCl_3$; Me_4Si): δ 7.40 (dd, ^3J(H,H) = 8.3 Hz, ^4J(H,H) = 1.9 Hz, 1H, Ar—H), 7.51 (d, ^4J(H,H) = 1.9 Hz, 1H^a, Ar—H), 7.75 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar—H), 9.23 (s, 1H, NH). ^{13}C NMR (125.75 MHz; $CDCl_3$; Me_4Si): δ 127.95 (s), 129.85 (d, ^3J(P,C) = 10.7 Hz), 130.83 (s), 131.91 (s), 132.53 (s), 139.44 (s), 164.30 (s, C=O).

*General Procedure for the Synthesis of Compounds **2–9**.* To a solution of 1 mmol of *N*-2,4-dichlorobenzoyl phosphoramidic dichloride (**1**) in dry acetonitrile at −5°C, 4 mmol of corresponding amine was added dropwise and the mixture was stirred for 6 h. After evaporating the solvent, the residue was washed with distilled water and acetonitrile and then recrystallized in a methanol/chloroform solution.

*N-2,4-Dichlorobenzoyl-N′,N″-bis(pyrrolidinyl) Phosphoric Triamide (**2**).* Yield: 88%. Decomposed at 238.9°C. Anal. Calcd. for $C_{15}H_{20}Cl_2N_3O_2P$ (%): C, 47.89; H, 5.36; N, 11.17. Found: C, 47.90; H, 5.35; N, 11.17. IR (KBr, cm^{-1}): ν_{max} = 3045 (s, NH), 2855 (s, CH_2), 1681 (s, C=O), 1576 (m), 1467 (s), 1281 (m), 1245 (s), 1209 (s, P=O), 1179 (s), 1121 (s), 1089 (s), 1045 (m), 1010 (m), 866 (m), 808 (m), 773 (m), 675 (m), 575 (s), 531 (m), 510 (m), 439 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 6.72 (m). ^{1}H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 1.78 (m, 8H, CH_2), 3.16 (m, 8H, CH_2), 7.47 (m, 2H, Ar—H), 7.66 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar—H), 9.38 (s, 1H, NH). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 25.81 (d, ^3J(P,C) = 7.9 Hz, CH_2), 45.81 (d, ^2J(P,C) = 4.0 Hz, CH_2), 127.16 (s), 128.89 (s), 130.00 (s), 130.67 (s), 134.60 (s), 135.59 (d, ^3J(P,C) = 8.1 Hz), 167.19 (s, C=O).

*N-2,4-Dichlorobenzoyl-N′,N″-bis(piperidinyl) Phosphoric Triamide (**3**).* Yield: 90%, m.p. = 229.4°C. Anal. Calcd. for $C_{17}H_{24}Cl_2N_3O_2P$ (%): C, 50.51; H, 5.98; N, 10.39. Found: C, 50.50; H, 5.98; N, 10.38. IR (KBr, cm^{-1}): ν_{max} = 3035 (s, NH), 2910 (s, CH_2), 1679 (s, C=O), 1576 (m), 1466 (s), 1444 (s), 1232 (m), 1208 (s, P=O), 1186 (s), 1163 (m), 1102 (m), 1071 (s), 955 (s), 849 (m), 805 (m), 773 (m), 720 (m), 575 (s), 439 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 8.67 (m). ^{1}H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 1.45 (m, 8H, CH_2), 1.51 (m, 4H, CH_2), 3.04 (m, 8H, CH_2), 7.41–7.48 (m, 2H, Ar—H), 7.66 (d, ^4J(H,H) = 1.6 Hz, 1H, Ar—H), 9.29 (s, 1H, NH). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 24.12 (s), 25.68 (d, ^3J(P,C) = 5.0 Hz, CH_2), 44.88 (d, ^2J(P,C) = 2.0 Hz, CH_2), 127.17 (s), 128.97 (s), 129.93 (s), 130.66 (s), 134.57 (s), 135.66 (s), 167.17 (s, C=O).

*N-2,4-Dichlorobenzoyl-N′,N″-bis(hexamethylenyl) Phosphoric Triamide (**4**).* Yield: 85%, m.p. = 181.8° C. Anal. Calcd. for $C_{19}H_{28}Cl_2N_3O_2P$ (%): C, 52.79; H, 6.53; N, 9.72. Found: C, 52.77; H, 6.52; N, 9.71. IR

(KBr, cm^{-1}): ν_{max} = 3425 (w, NH), 3050 (m, CH_2), 2900 (s, CH_2), 1674 (s, C=O), 1575 (m), 1435 (s), 1380 (m), 1283 (m), 1228 (m), 1186 (s, P=O), 1150 (m), 1089 (m), 1057 (s), 940 (m), 895 (m), 871 (m), 772 (m), 750 (m), 700 (m), 571 (w), 439 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 12.41 (m). ^1H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 1.60 (m, 16H, CH_2), 3.14 (m, 8H, CH_2), 7.41 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar—H), 7.49 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.9 Hz, 1H, Ar—H), 7.66 (d, ^4J(H,H) = 1.9 Hz, 1H, Ar—H), 9.32 (s, 1H, NH). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 26.28 (s, CH_2), 29.71 (d, ^3J(P,C) = 3.9 Hz, CH_2), 46.92 (d, ^2J(P,C) = 4.5 Hz, CH_2), 127.19 (s), 129.02 (s), 129.89 (s), 130.69 (s), 134.59 (s), 135.66 (d, ^3J(P,C) = 9.3 Hz), 167.10 (s, C=O).

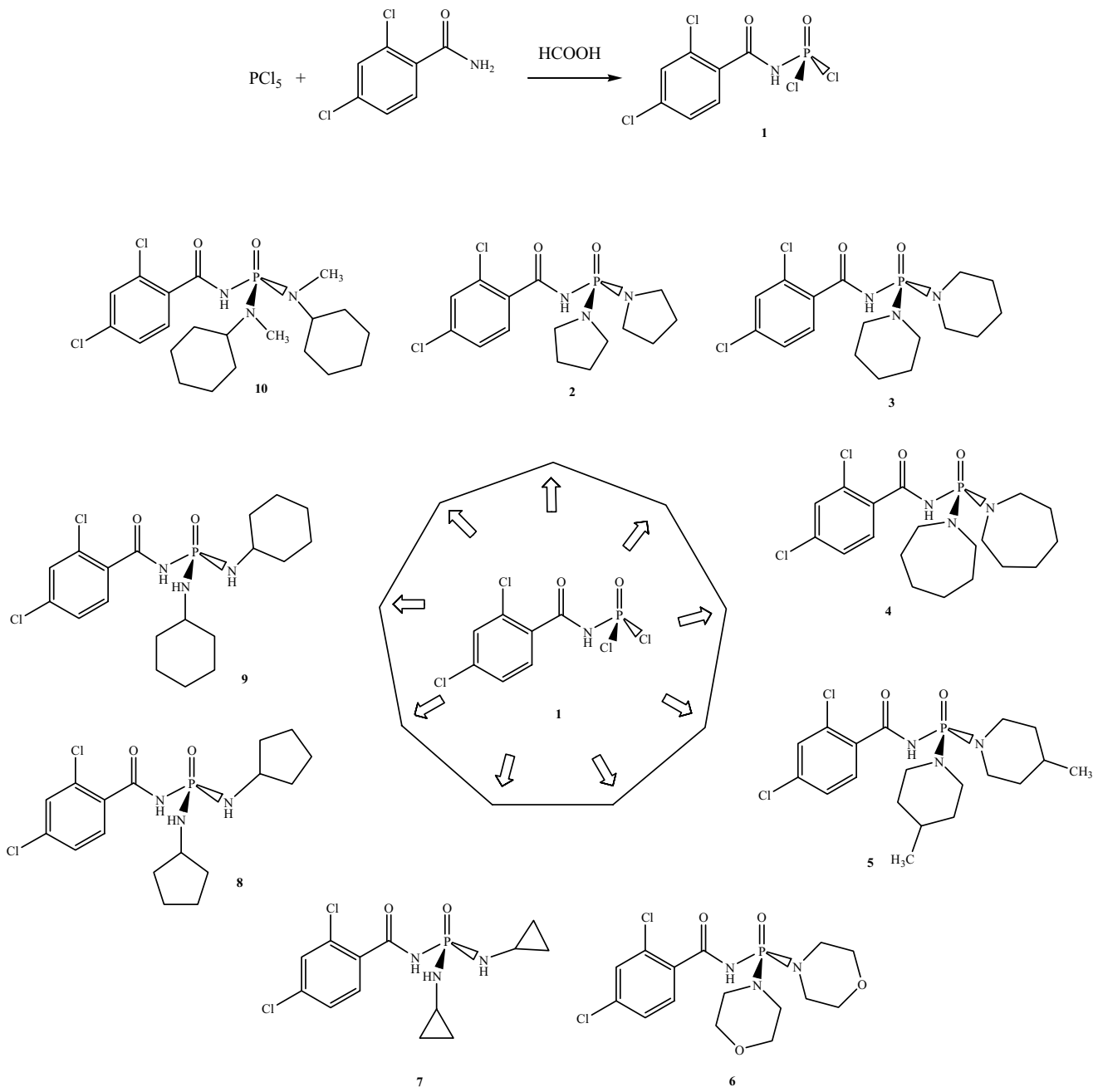
*N-2,4-Dichlorobenzoyl-N′,N″-bis(4-methyl piperidinyl) Phosphoric Triamide (**5**).* Yield: 80%, m.p. = 184.5°C. Anal. Calcd. for $C_{19}H_{28}Cl_2N_3O_2P$ (%): C, 52.79; H, 6.53; N, 9.72. Found: C, 52.78; H, 6.53; N, 9.71. IR (KBr, cm^{-1}): ν_{max} = 3475 (w, NH), 3095 (m), 2920 (s, CH), 1693 (s, C=O), 1580 (m), 1440 (vs, C=C), 1375 (m), 1343 (w), 1280 (m), 1249 (m), 1195 (s, P=O), 1160 (m), 1116 (m), 1063 (s), 959 (m), 939 (s), 868 (m), 810 (m), 777 (m), 753 (m), 508 (m), 449 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 8.72 (m). ^1H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 0.88 (d, ^3J(H,H) = 6.5 Hz, 6H, CH_3), 1.04 (m, 4H), 1.44 (m, 2H), 1.55 (d, ^2J(H,H) = 12.1 Hz, 4H), 2.59–2.66 (m, 4H), 3.48 (m, 4H), 7.41 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar—H), 7.47 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.9 Hz, 1H, Ar—H), 7.66 (d, ^4J(H,H) = 1.9 Hz, 1H, Ar—H), 9.40 (^2J(PNH) = 7.5 Hz, 1H, NH_{amide}). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 22.02 (s, CH_3), 30.44 (s, CH), 34.03 (d, ^3J(P,C) = 5.0 Hz, CH_2), 34.13 (d, ^3J(P,C) = 5.0 Hz, CH_2), 42.20 (d, ^2J(P,C) = 2.3 Hz, CH_2), 44.38 (d, ^2J(P,C) = 2.6 Hz, CH_2), 127.21 (s), 129.01 (s), 130.68 (s), 134.62 (s), 135.62 (d, ^3J(P,C) = 8.9 Hz), 167.17 (s, C=O).

*N - 2,4 - Dichlorobenzoyl - N′,N″ - bis(morpholinyl) Phosphoric Triamide (**6**).* Yield: 83%, m.p. = 238.0°C. Anal. Calcd. for $C_{15}H_{20}Cl_2N_3O_4P$ (%): C, 44.13; H, 4.94; N, 10.29. Found: C, 44.12; H, 4.95; N, 10.30. IR (KBr, cm^{-1}): ν_{max} = 3410 (m, NH), 3040 (m, CH_2), 2850 (m, CH_2), 1673 (s, C=O), 1576 (m), 1452 (s), 1371 (m), 1286 (m), 1254 (m), 1187 (s, P=O), 1110 (s), 1087 (m), 967 (s), 910 (m), 866 (m), 823 (m), 744 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 8.90 (m). ^1H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 3.09 (m, 8H, CH_2), 3.55 (t, ^3J(H,H) = 4.5 Hz, 8H, CH_2), 7.49 (m, 2H, Ar—H), 7.68 (d, ^4J(H,H) = 1.6 Hz, 1H, Ar—H), 9.65 (s, 1H, NH). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 44.31 (s, CH_2), 66.34 (d, ^3J(P,C) = 5.6 Hz, CH_2), 127.23 (s), 129.04 (s), 130.72 (s), 134.87 (s), 135.23 (d, ^3J(P,C) = 9.3 Hz), 167.44 (s, C=O).

*N - 2,4 - Dichlorobenzoyl - N′,N″ - bis(cyclopropyl) Phosphoric Triamide (**7**).* Yield: 73%, m.p. = 164.8°C. Anal. Calcd. for $C_{13}H_{16}Cl_2N_3O_2P$ (%): C, 44.85; H, 4.63; N, 12.07. Found: C, 44.84; H, 4.63; N, 12.06. IR (KBr, cm^{-1}): ν_{max} = 3265 (s, NH), 3100 (m, CH), 2910 (w), 1656 (s, C=O), 1585 (m), 1438 (s), 1355 (s), 1274 (m), 1240 (m), 1201 (s, P=O), 1169 (w), 1133 (m), 1100 (m), 1045 (m), 1023 (m), 969 (m), 891 (s), 865 (m), 833 (m), 772 (s), 709 (w), 689 (m), 621 (w), 570 (m), 508 (m), 430 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 6.54 (m). ^1H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 0.43–0.54 (m, 8H, CH_2), 2.30 (m, 2H), 4.74 (d, ^2J(PNH) = 11.7 Hz, 2H, NH_{amine}), 7.44–7.49 (m, 2H, Ar—H), 7.65 (d, ^4J(H,H) = 1.6 Hz, 1H, Ar—H), 9.47 (d, ^2J(PNH) = 7.0 Hz, 1H, NH_{amide}). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 6.15 (d, ^3J(P,C) = 6.3 Hz, CH_2), 6.25 (d, ^3J(P,C) = 5.1 Hz, CH_2), 22.12 (s, CH), 127.12 (s), 129.06 (s), 130.17 (s), 130.84 (s), 134.64 (s), 135.36 (d, ^3J(P,C) = 8.5 Hz), 167.03 (s, C=O).

*N - 2,4 - Dichlorobenzoyl - N′,N″ - bis(cyclopentyl) Phosphoric Triamide (**8**).* Yield: 75%, m.p. = 222.2°C. Anal. Calcd. for $C_{17}H_{24}Cl_2N_3O_2P$ (%): C, 50.51; H, 5.98; N, 10.39. Found: C, 50.49; H, 5.98; N, 10.40. IR (KBr, cm^{-1}): ν_{max} = 3370 (s, NH), 3060 (s), 3000 (s), 2870 (s), 1659 (s, C=O), 1582 (m), 1552 (w), 1474 (s), 1437 (s, C—C), 1372 (w), 1287 (m), 1208 (vs, P=O), 1176 (m), 1106 (m), 1049 (m), 947 (m), 912 (m), 876 (m), 844 (m), 811 (m), 769 (m), 700 (w), 568 (w), 511 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 5.25 (m). ^1H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 1.42 (m, 8H), 1.60 (m, 4H), 1.75 (m, 4H), 3.47 (m, 2H), 4.25 (dd, ^2J(PNH) = 9.3 Hz, ^3J(H,H) = 8.8 Hz, 2H, NH_{amine}), 7.43 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar—H), 7.47 (d, ^3J(H,H) = 8.5 Hz, 1H, Ar—H), 7.62 (s, 1H, Ar—H), 9.46 (s, 1H, NH_{amide}). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 22.79 (s, CH_2), 22.90 (s, CH_2), 34.02 (d, ^3J(P,C) = 5.0 Hz, CH_2), 34.23 (d, ^3J(P,C) = 6.4 Hz, CH_2), 51.92 (s, CH), 127.13 (s), 129.11 (s), 130.19 (s), 130.91 (s), 134.66 (s), 135.26 (d, ^3J(P,C) = 8.6 Hz), 166.89 (s, C=O).

*N - 2, 4 - Dichlorobenzoyl - N′, N″ - bis(cyclohexyl) Phosphoric Triamide (**9**).* Yield: 82%, m.p. = 215.5°C. Anal. Calcd. for $C_{19}H_{28}Cl_2N_3O_2P$ (%): C, 52.79; H, 6.53; N, 9.72. Found: C, 52.78; H, 6.53; N, 9.72. IR (KBr, cm^{-1}): ν_{max} = 3415 (m, NH), 3240 (s, NH), 2905 (s, CH_2), 1649 (s, C=O), 1579 (m),



SCHEME 1 The preparation pathway for the synthesis of compounds **1–10**.

1432 (s), 1277 (m), 1235 (m), 1201 (m, P=O), 1125 (m), 1094 (s), 917 (m), 879 (m), 766 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 5.59 (m). ^{1}H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 1.16–2.10 (m, 20H), 2.94 (s, 2H), 4.16 (s, 2H, NH_{amine}), 7.49 (m, 3H, Ar—H), 8.85 (b, 1H, NH_{amide}). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 24.74 (s), 25.09 (s), 34.95 (s), 35.34 (s), 49.21 (s), 127.19 (s), 129.08 (s), 130.02 (s), 130.76 (s), 134.57 (s), 135.40 (s), 166.91 (s, C=O).

*N-2,4-Dichlorobenzoyl-N′,N″-bis(N-methylcyclohexyl) Phosphoric Triamide (***10***).* To a solution of 1 mmol of *N*-2,4-dichlorobenzoyl phosphoramidic dichloride (**1**) in dry chloroform at −5°C, a mixture of *N*-methylcyclohexylamine (2 mmol) and triethylamine (2 mmol) was added dropwise and stirred for 4 h. After evaporating the solvent, the residue was washed with distilled water and acetonitrile and then recrystallized in a methanol/chloroform solution.

TABLE 1 Some Spectroscopic Data of Compounds **1–10** and Their Analogues

Compound	$\delta(^{31}P)$ (ppm)	^{2}J(PNH) (Hz)	^{4}J(H,H) (Hz)	^{2}J(P,C)-aliphatic (Hz)	^{3}J(P,C)-aliphatic (Hz)	^{3}J(P,C)-aromatic (Hz)	ν(P=O) (cm^{-1})	ν(C=O) (cm^{-1})	Ref.
2,4-Cl_2-C_6H_3-C(O)NHP(O)Cl_2 (**1**)	5.99	–	1.9	–	—	10.7	1227	1707	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NC_4H_8)_2$ (**2**)	6.72	–	1.5	4.0	7.9	8.1	1209	1681	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NC_5H_{10})_2$ (**3**)	8.67	–	1.6	2.0	5.0	–	1208	1679	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NC_6H_{12})_2$ (**4**)	12.41	–	1.9	4.5	3.9	9.3	1186	1674	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(4\text{-}CH_3\text{-}NC_5H_9)_2$ (**5**)	8.72	7.5 (amide)	1.9	2.3, 2.6	5.0, 5.0	8.9	1195	1693	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NC_4H_8O)_2$ (**6**)	8.90	–	1.6	–	5.6	9.3	1187	1673	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NHC_3H_5)_2$ (**7**)	6.54	11.7 (amine) 7.0 (amide)	1.6	–	5.1, 6.3	8.5	1201	1656	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NHC_5H_9)_2$ (**8**)	5.25	9.3 (amine)	–	–	5.0, 6.4	8.6	1208	1659	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$(NHC_6H_{11})_2$ (**9**)	5.59	–	–	–	–	–	1201	1649	a,b
2,4-Cl_2-C_6H_3-C(O)NHP(O)$[N(CH_3)(C_6H_{11})]_2$ (**10**)	11.96	–	–	3.1	–	–	1178	1682	a,b
4-Cl-C_6H_4-C(O)NHP(O)Cl_2 (**11**)	10.52	12.0 (amide)	–	5.4 (C=O)	–	9.8	1226	1683	26c
4-Cl-C_6H_4-C(O)NHP(O)$(NC_5H_{10})_2$ (**12**)	11.64	3.2 (amide)	–	2.8 1.9 (C=O)	5.9	7.3	1207	1667	26c
4-Cl-C_6H_4-C(O)NHP(O)$(NC_4H_8O)_2$ (**13**)	10.87	5.5 (amide)	–	4.5 1.9 (C=O)	1.1	6.3	1193	1666	29c
4-Cl-C_6H_4-C(O)NHP(O)$(NC_6H_{12})_2$ (**14**)	14.42	–	–	4.7	2.9	8.5	1178	1660	28
4-Cl-C_6H_4-C(O)NHP(O)$(NHC_3H_5)_2$ (**15**)	10.56	5.0 (amide)	–	–	5.8, 5.1	–	1205	1642	28c
4-Cl-C_6H_4-C(O)NHP(O)$(NHC_5H_9)_2$ (**16**)	8.86	5.1 (amide)	–	–	7.0, 4.7	7.8	1218	1621	27c
4-Cl-C_6H_4-C(O)NHP(O)$(NHC_6H_{11})_2$ (**17**)	6.21	4.1 (amide)	–	6.3 1.8 (C=O)	10.1, 3.8	5.3	1215	1635	26c
C_6H_5-C(O)NHP(O)$(NC_4H_8)_2$ (**18**)	8.84	–	–	5.5	8.6	8.7	1202	1665	42c
C_6H_5-C(O)NHP(O)$(NC_5H_{10})_2$ (**19**)	12.02	–	–	4.7 3.9 (C=O)	4.7	8.5	1203	1667	41c
C_6H_5-C(O)NHP(O)$(NC_6H_{12})_2$ (**20**)	14.70	3.8 (amide)	–	4.7	4.2	8.7	1182	1660	43c
C_6H_5-C(O)NHP(O)$(4\text{-}CH_3\text{-}NC_5H_9)_2$ (**21**)	12.13	–	–	2.9, 0.0	4.9, 5.1	8.5	1190	1668	41c
C_6H_5-C(O)NHP(O)$(NHC_3H_5)_2$ (**22**)	8.80	–	–	–	5.9, 4.9	–	1202	1635	28c
C_6H_5-C(O)NHP(O)$(NHC_5H_9)_2$(**23**)	8.99	–	–	–	4.8, 6.2	8.1	1204	1637	27c
C_6H_5-C(O)NHP(O)$(NHC_6H_{11})_2$ (**24**)	7.85	5.5 (amide)	–	6.4 3.4 (C=O)	3.9	6.5	1205	1630	26c
C_6H_5-C(O)NHP(O)$[N(CH_3)(C_6H_{11})]_2$ (**25**)	13.56	5.9 (amide)	–	5.2, 4.8 2.9 (C=O)	3.1, 3.9	8.6	1183	1670	44b

[a]This work.
[b]NMR solvent is d_6-DMSO.
[c]NMR solvent is $CDCl_3$.

Yield: 78%, m.p. = 180.3°C. Anal. Calcd. for $C_{21}H_{32}Cl_2N_3O_2P$ (%): C, 54.79; H, 7.01; N, 9.13. Found: C, 54.78; H, 7.00; N, 9.12. IR (KBr, cm^{-1}): ν_{max} = 3050 (m, CH_2), 2905 (s, CH_2), 1682 (s, C=O), 1575 (m), 1460 (s), 1431 (s), 1383 (m), 1268 (m), 1221 (m), 1178 (s, P=O), 1154 (m), 1099 (m), 1044 (m), 1000 (s), 974 (s), 849 (s), 809 (m), 770 (m), 747 (m), 571 (m), 538 (m), 503 (m). ^{31}P NMR (202.46 MHz; d_6-DMSO; 85% H_3PO_4): δ 11.96 (m). ^{1}H NMR (500.13 MHz; d_6-DMSO; Me_4Si): δ 1.03 (s, 3H, N-CH_3), 1.22 (s, 3H, N-CH_3), 1.48–1.72 (m, 16H), 3.28 (s, 6H), 7.38 (d, ^{3}J(H,H) = 6.6 Hz, 1H, Ar—H), 7.47 (d, ^{3}J(H,H) = 6.6 Hz, 1H, Ar—H), 7.66 (s, 1H, Ar—H), 9.31 (s, 1H, NH). ^{13}C NMR (125.75 MHz; d_6-DMSO; Me_4Si): δ 25.06 (s), 25.63 (s), 27.27 (d, ^{2}J(P,C) = 3.1 Hz), 20.23 (s), 30.34 (s), 54.08 (s), 127.20 (s), 128.28 (s), 129.82 (s), 130.66 (s), 134.54 (s), 135.77 (s), 167.01 (s, C=O).

RESULTS AND DISCUSSION

Spectroscopic Study

From the reaction of PCl_5 with 2,4-dichlorobenzamide and then oxidation with formic acid, compound *N*-2,4-$Cl_2C_6H_3C(O)NHP(O)Cl_2$ (**1**) was obtained as a new intermediate that interacted with various amines to yield several new phosphoric triamides **2–10** (Scheme 1). Spectroscopic data of these compounds and their analogues *N*-4-$ClC_6H_4C(O)NHP(O)X_2$ and $C_6H_5C(O)NHP(O)X_2$,

TABLE 2 Crystallographic Data for Compounds **3, 4,** and **10**

	3	**4**	**10**
Empirical formula	$C_{17}H_{24}Cl_2N_3O_2P$	$C_{19}H_{28}Cl_2N_3O_2P$	$C_{21}H_{32}Cl_2N_3O_2P$
Formula weight	404.26	432.31	460.37
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, *P*-1	Orthorhombic, *Pbca*	Monoclinic, *P*21/*c*
Unit cell dimensions			
a (Å)	9.9189(6)	18.5102(7)	10.463(2)
b (Å)	10.1898(7)	10.4647(6)	21.076(4)
c (Å)	11.0809(7)	21.4451(11)	10.4944(19)
α (°)	103.9600(10)	90	90
β (°)	116.3000(10)	90	102.139(6)
γ (°)	92.3010(10)	90	90
V (Å^3)	960.36(11)	4154.0(4)	2262.5(7)
Z, calculated density (Mg m^{-3})	2, 1.398	8, 1.383	4, 1.352
Absorption coefficient (mm^{-1})	0.437	0.409	0.380
F(000)	424	1824	976
Crystal size (mm)	0.55 × 0.40 × 0.30	0.30 × 0.20 × 0.15	0.30 × 0.10 × 0.08
θ range for data collection (°)	2.09–28.00	1.90–29.99	1.93–26.00
Limiting indices	$-13 \le h \le 13$ $-13 \le k \le 13$ $-14 \le l \le 14$	$-25 \le h \le 26$ $-14 \le k \le 14$ $-30 \le l \le 30$	$-12 \le h \le 8$ $-25 \le k \le 25$ $-12 \le l \le 12$
Reflections collected/unique	9,926/4,609 [*R*(int) = 0.0188]	45,607/6,037 [*R*(int) = 0.0746]	10,668/4,405 [*R*(int) = 0.0347]
Completeness to θ	99.4%	99.6%	99.2%
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents	Semiempirical from equivalents
Max. and min. transmission	0.858 and 0.847	0.943 and 0.884	0.968 and 0.957
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4609/0/230	6037/0/244	4405/1/268
Goodness-of-fit on F^2	1.012	1.009	1.003
Final *R* indices	$R_1 = 0.0330$, $wR_2 = 0.0858$	$R_1 = 0.0574$, $wR_2 = 0.1280$	$R_1 = 0.0627$, $wR_2 = 0.1196$
R indices (all data)	$R_1 = 0.0361$, $wR_2 = 0.0886$	$R_1 = 0.0789$, $wR_2 = 0.1375$	$R_1 = 0.0931$, $wR_2 = 0.1301$
Largest diff. peak and hole (e Å^{-3})	0.382 and −0.457	0.675 and −0.385	0.531 and −0.837

where X = amine, have been summarized in Table 1. ^{31}P NMR spectra indicate that $\delta(^{31}P)$ shifts to down fields with increasing ring sizes of amine groups from five to seven members in molecules **2–4**. Similar results were obtained for their analogues **12** and **14**. In both sets of compounds **2–4** (with N atom as a ring member) and **7–10** (with N atom out of the ring) for molecules with the biggest amine group (**4** and **10**), $\delta(^{31}P)$ is the most downfield. Results show that among compounds **1–25**, the *N*-2,4-dichlorobenzoyl derivatives have the most upfield $\delta(^{31}P)$ in comparison with their *N*-4-chlorobenzoyl and *N*-enzoyl analogues.

It is noteworthy that the reaction of compound **6** with $SnCl_2(CH_3)_2$ in 2:1 molar ratio in a methanol/chloroform mixture gave its polymorph **6a**. It must be noted that several parameters such as solvent, certain impurities or additives, concentration, temperature, the geometry of covalent bonds, and the stirring conditions [36,37], affect the formation of a polymorph. Here, $SnCl_2(CH_3)_2$ acts as an additive and helps in the formation of polymorph **6a**. The NMR and IR spectra of **6** and **6a** do not indicate remarkable differences and are nearly the same.

Interestingly, the ^{1}H NMR spectra of molecules **1–7** display long-range ^4J(H,H) coupling constants (range = 1.5–1.9 Hz) for the coupling of aromatic protons in 2,4-dichlorophenyl rings. Typically, ^4J(H,H) coupling constants for the phenyl rings are in the range of 1 to 3 Hz and the particular values seem to depend as much on the pattern of substitution as the nature of the substituent [38]. This coupling was not observed

TABLE 3 Crystallographic Data for Compounds **6** and **6a**

	6	**6a**
Empirical formula	$C_{15}H_{20}Cl_2N_3O_4P$	$C_{15}H_{20}Cl_2N_3O_4P$
Formula weight	408.21	408.21
Temperature (K)	120(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P-1
Unit cell dimensions		
a (Å)	9.3320(6)	9.7293(6)
b (Å)	10.2359(7)	10.2201(7)
c (Å)	19.0063(13)	10.9196(7)
α (°)	90	105.599(1)
β (°)	91.132(2)	103.461(1)
γ (°)	90	110.791(1)
V (Å^3)	1815.2(2)	910.42(10)
Z, Calculated density (Mg m^{-3})	4, 1.494	2, 1.489
Absorption coefficient (mm^{-1})	0.472	0.470
F(000)	848	424
Crystal size (mm)	0.35 × 0.25 × 0.20	0.45 × 0.37 × 0.20
θ range for data collection (°)	2.14 to 29.00	2.08 to 25.99
Limiting indices	$-12 \le h \le 12$, $-13 \le k \le 13$, $-24 \le l \le 25$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-12 \le l \le 13$
Reflections collected/unique	19,475/4,785 [R(int) = 0.0598]	6,175/3,537 [R(int) = 0.0171]
Completeness to θ	99.3%	98.9%
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents
Max. and min. transmission	0.907 and 0.856	0.912 and 0.816
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4785/0/262	3537/0/230
Goodness-of-fit on F^2	0.972	1.015
Final R indices	$R_1 = 0.0505$, $wR_2 = 0.0890$	$R_1 = 0.0369$, $wR_2 = 0.0941$
R indices (all data)	$R_1 = 0.1062$, $wR_2 = 0.1006$	$R_1 = 0.0423$, $wR_2 = 0.0979$
Largest diff. peak and hole (e Å^{-3})	0.353 and −0.575	1.545 and −0.360

TABLE 4 Selected Bond Lengths (Å) and Angles (°) for Compounds **3, 4,** and **10**

3		**4**		**10**	
P(1)—O(1)	1.4858(9)	P(1)—O(1)	1.4795(16)	P(1)—O(1)	1.485(2)
P(1)—N(1)	1.6852(11)	P(1)—N(1)	1.6283(18)	P(1)—N(1)	1.693(3)
P(1)—N(2)	1.6335(11)	P(1)—N(2)	1.6445(18)	P(1)—N(2)	1.629(3)
P(1)—N(3)	1.6322(11)	P(1)—N(3)	1.6908(18)	P(1)—N(3)	1.633(3)
O(2)—C(1)	1.2183(16)	O(2)—C(13)	1.222(2)	O(2)—C(1)	1.212(4)
N(1)—C(1)	1.3733(16)	N(3)—C(13)	1.372(3)	N(1)—C(1)	1.370(4)
Cl(1)—C(3)	1.7365(13)	C(15)—Cl(1)	1.735(2)	C(3)—Cl(1)	1.732(4)
Cl(2)—C(5)	1.7357(13)	C(17)—Cl(2)	1.734(2)	C(5)—Cl(2)	1.738(3)
O(1)—P(1)—N(1)	106.76(5)	O(1)—P(1)—N(1)	115.10(10)	O(1)—P(1)—N(1)	105.89(14)
O(1)—P(1)—N(2)	113.62(6)	O(1)—P(1)—N(2)	110.22(10)	O(1)—P(1)—N(2)	110.92(15)
O(1)—P(1)—N(3)	110.66(5)	O(1)—P(1)—N(3)	106.93(9)	O(1)—P(1)—N(3)	118.35(15)
N(2)—P(1)—N(1)	106.57(5)	N(2)—P(1)—N(1)	108.06(9)	N(2)—P(1)—N(1)	111.62(15)
N(3)—P(1)—N(1)	110.53(6)	N(1)—P(1)—N(3)	107.33(9)	N(1)—P(1)—N(3)	105.52(15)
N(3)—P(1)—N(2)	108.62(6)	N(2)—P(1)—N(3)	109.03(9)	N(2)—P(1)—N(3)	104.50(15)
C(1)—N(1)—P(1)	126.93(9)	C(13)—N(3)—P(1)	124.47(15)	C(1)—N(1)—P(1)	125.8(2)
C(1)—N(1)—H(1N)	117.6(12)	C(13)—N(3)—H(3N)	116.4	C(1)—N(1)—H(1N)	119(2)
P(1)—N(1)—H(1N)	115.3(12)	P(1)—N(3)—H(3N)	118.5	P(1)—N(1)—H(1N)	115(2)

TABLE 5 Selected Bond Lengths (Å) and Angles (°) for Compounds **6** and **6a**

	6	**6a**
P(1)—O(2)	1.479(2)	1.4820(15)
P(1)—N(1)	1.682(2)	1.6826(18)
P(1)—N(2)	1.633(2)	1.6380(17)
P(1)—N(3)	1.631(2)	1.6340(18)
O(1)—C(1)	1.219(3)	1.219(3)
N(1)—C(1)	1.370(4)	1.365(3)
N(3)—C(12)	1.554(10)	1.480(3)
N(3)—C(12′)	1.447(10)	–
O(2)—P(1)—N(1)	107.17(11)	106.34(9)
O(2)—P(1)—N(2)	115.12(12)	109.85(8)
O(2)—P(1)—N(3)	110.59(12)	117.94(9)
N(2)—P(1)—N(1)	106.17(12)	111.68(9)
N(1)—P(1)—N(3)	110.87(12)	107.00(9)
N(2)—P(1)—N(3)	106.85(11)	104.08(9)
C(1)—N(1)—P(1)	126.07(17)	127.31(15)
C(1)—N(1)—H(1N)	126.7	116.1(17)
P(1)—N(1)—H(1N)	107.1	116.0(17)

TABLE 6 Selected Torsion Angles (°) for Compounds **6** and **6a**

	6	**6a**
O(2)—P(1)—N(1)—C(1)	−160.5(2)	−161.34(17)
O(2)—P(1)—N(2)—C(8)	−131.5(2)	44.46(18)
O(2)—P(1)—N(2)—C(11)	51.8(2)	−160.73(17)
O(2)—P(1)—N(3)—C(15)	−149.3(3)	−94.69(18)
O(2)—P(1)—N(3)—C(12)	20.3(4)	50.09(18)
O(1)—C(1)—C(2)—C(7)	134.3(3)	−53.2(3)
O(1)—C(1)—C(2)—C(3)	−42.2(4)	125.5(2)
P(1)—N(1)—C(1)—O(1)	−12.1(4)	−17.0(3)
P(1)—N(1)—C(1)—C(2)	166.14(18)	164.64(14)
P(1)—N(2)—C(11)—C(10)	−126.9(2)	146.77(16)
N(1)—P(1)—N(2)—C(8)	−13.1(3)	−73.27(17)
N(1)—P(1)—N(2)—C(11)	170.22(19)	81.53(19)
N(2)—P(1)—N(1)—C(1)	76.0(2)	−41.5(2)
N(2)—P(1)—N(3)—C(15)	−23.3(3)	143.35(17)
N(3)—P(1)—N(1)—C(1)	−39.7(3)	71.77(19)
N(3)—P(1)—N(2)—C(8)	105.3(2)	171.63(15)
N(3)—P(1)—N(2)—C(11)	−71.4(2)	−33.56(19)

for our previously reported phosphoric triamides [23,26–29].

It is shown in Table 1 that among molecules **1–25**, compound **1** has the highest $^{3}J(\mathrm{P,C})_{\mathrm{aromatic}}$, ν(P=O) and ν(C=O) values. These results are mainly due to the presence of two electronegative Cl atoms on the phenyl ring as well as two Cl atoms connected to the phosphorus atom. ^{13}C NMR spectra of compounds **5, 7, 8, 9, 10,** and **21** exhibit that all the aliphatic carbon atoms of amino moieties are unequal and indicate different signals. ^{13}C NMR spectra illustrate the ^{2}J(P,C=O) values between 1.8 and 3.9 Hz for some benzoyl and 4-chlorobenzoyl compounds, whereas this constant was not observed for their 2,4-dicholorobenzoyl analogues. As the aliphatic ring size increases from 2 to 4, the ν(P=O), ν(C=O), and $^{3}J(\mathrm{P,C})_{\mathrm{aliphatic}}$ values decrease. It is notable that the ν(C=O) values are the largest ones in

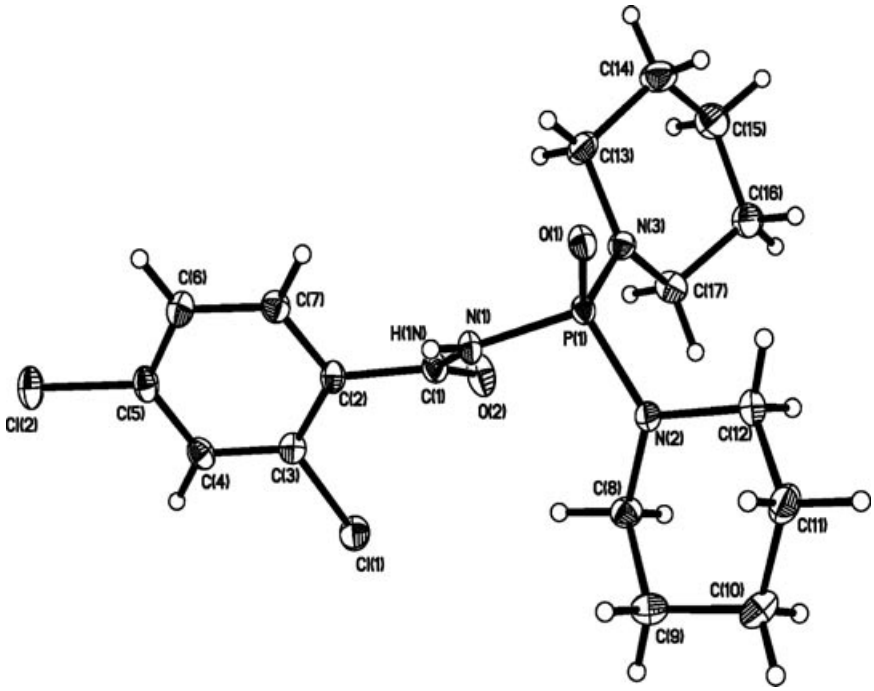


FIGURE 1 Molecular structure and atom-labeling scheme for compound **3** (50% probability ellipsoids).

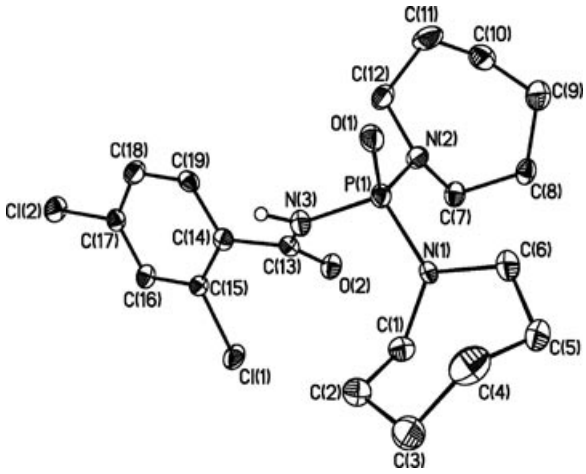


FIGURE 2 Molecular structure and atom-labeling scheme for compound **4** (50% probability ellipsoids).

N-2,4-dichlorobenzoyl phosphoramidates relative to the values of their *N*-4-chlorobenzoyl and *N*-benzoyl analogues, which can be attributed to an increase in the number of electronegative chlorine atoms on the phenyl ring.

X-ray Crystallography

Single crystals of compounds **3, 4, 6**, **6a**, and **10** were obtained from a mixture of methanol/chloroform at room temperature. The crystal data and the details of the X-ray analysis are given in Tables 2 and 3. Selected bond lengths and angles are presented in Tables 4 and 5, and molecular structures (ORTEP view) are shown in Figs. 1–5.

In compound **4**, seven-membered aliphatic rings demonstrate a puckered shape, and in molecules **3, 6, 6a**, and **10**, the six-membered rings have stable chair conformation. The interesting point about structures **6** and **6a** is that they are polymorphic. The polymorph **6a** was acquired by adding $SnCl_2(CH_3)_2$ to a solution of **6**. The polymorphs **6** and **6a** crystallize in monoclinic and triclinic systems, with $Z = 4$ and 2, respectively. It could be seen from the ORTEP figures that disorder in **6** has disappeared in **6a**. The bond lengths and bond angles of these structures are nearly identical, but their similar torsion angles exhibit great differences (Table 6). Also, there are some differences in their hydrogen bondings, that is, the H···A distance in **6** is shorter than that of **6a**, exhibiting a stronger H-bond in this compound (Table 7).

In all of these structures, the phosphoryl and carbonyl groups indicate anticonfigurations and the phosphorus atoms have distorted tetrahedral configuration. The bond angles around P(1) atoms in these compounds are in the range from 104.08(9)° to 118.35(15)°.

The P—N_{amide} bond lengths (about 1.69 Å) are longer than the P—N_{amine} bonds (about 1.63 Å) because of the resonance interaction of N_{amide} with the C=O π system, which cause a partial multiple bond character in C—N_{amide} (the C—N_{amide} bond lengths are shorter than the C—N_{amine} bond lengths; Tables 4 and 5). All of the P—N bonds are shorter than the typical

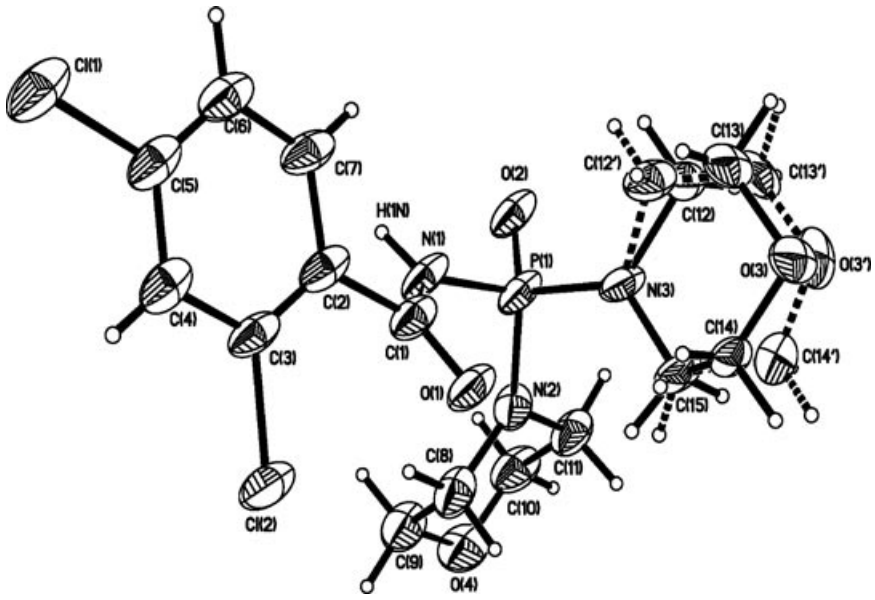


FIGURE 3 Molecular structure and atom-labeling scheme for compound **6** (50% probability ellipsoids).

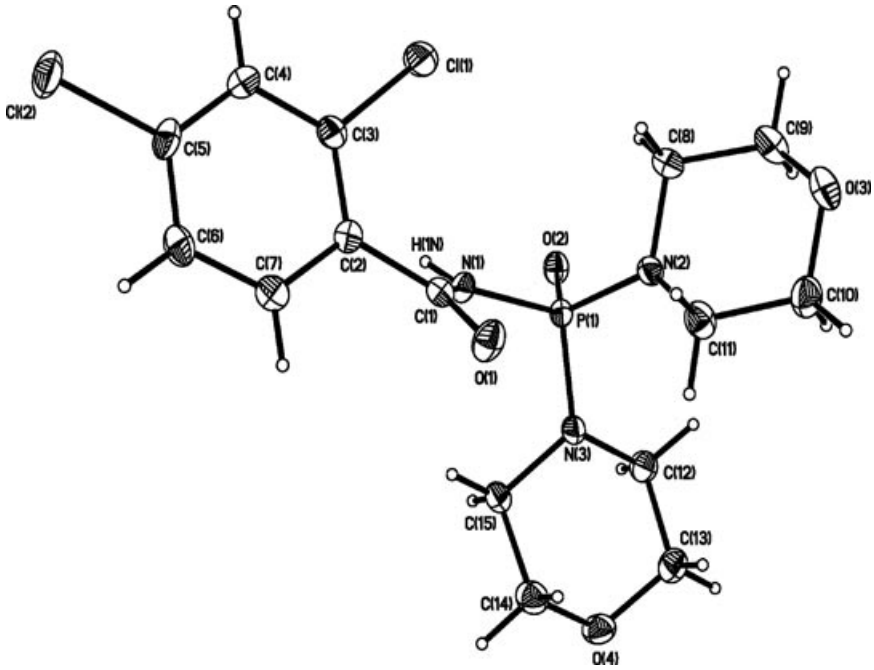


FIGURE 4 Molecular structure and atom-labeling scheme for compound **6a** (50% probability ellipsoids).

P—N single bond (1.77 Å) [39]. This is probably due to the electrostatic effects of polar bonds that overlap with P—N sigma bond [40]. The P=O bond lengths in these compounds are larger than the normal P=O bond length (1.45 Å) [39].

The environment around the nitrogen atoms is practically planar. For example, in compound **4**, the angles C(7)—N(2)—C(12), C(7)—N(2)—P(1), and C(12)—N(2)—P(1) are 114.60(18)°, 124.00(15)°, and 115.56(15)°, respectively, with average of 118.05°. The sum of surrounding angles around N(1), N(2), and N(3) atoms are 359.96°, 354.16°, and 359.37°, respectively. Similar results were obtained for the nitrogen atoms of other structures, which confirm the sp^2 hybridization of the N atoms, although because of the repulsion and steric interactions, some angles are larger and others are smaller than 120°. This observation suggests the existence of a partial multiple bond between phosphorus and nitrogen atoms, which has already been confirmed by the crystallographic data of our previously reported similar compounds [22,23,26–29].

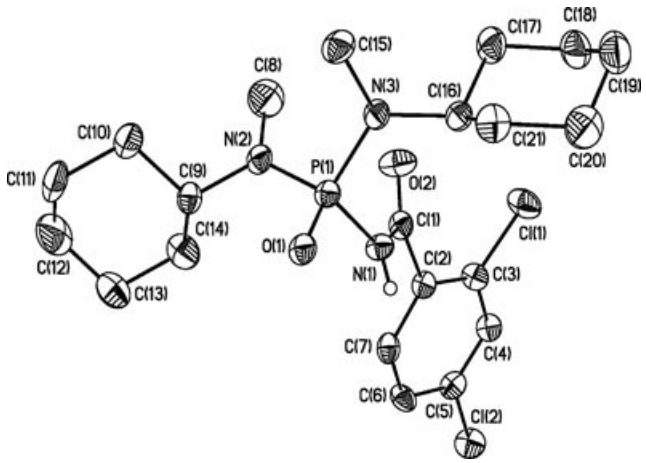


FIGURE 5 Molecular structure and atom-labeling scheme for compound **10** (50% probability ellipsoids).

These structures contain one amidic hydrogen atom and form dimers through intermolecular —P=O···H—N— hydrogen bonds (Table 7), which are centrosymmetric for all of them except for **6** (owing to its disorder). Beside these H-bonds, there are also weak C—H···O and C—H···Cl hydrogen bonds in the crystalline network, which produce a two-dimensional polymeric chain in the crystal lattice of **4** (Fig. 6) and three-dimensional polymers for others (e.g., see Fig. 7 for **10**). There are also π-π stacking of two phenyl rings, with C—C distances in the range of 3.292 to 3.444 Å in these structures. Moreover, in structure **4**, there are intramolecular electrostatic interactions between O(2) of C=O group and *ortho* Cl(1) atoms as well as O(2) and N(2) atoms, with

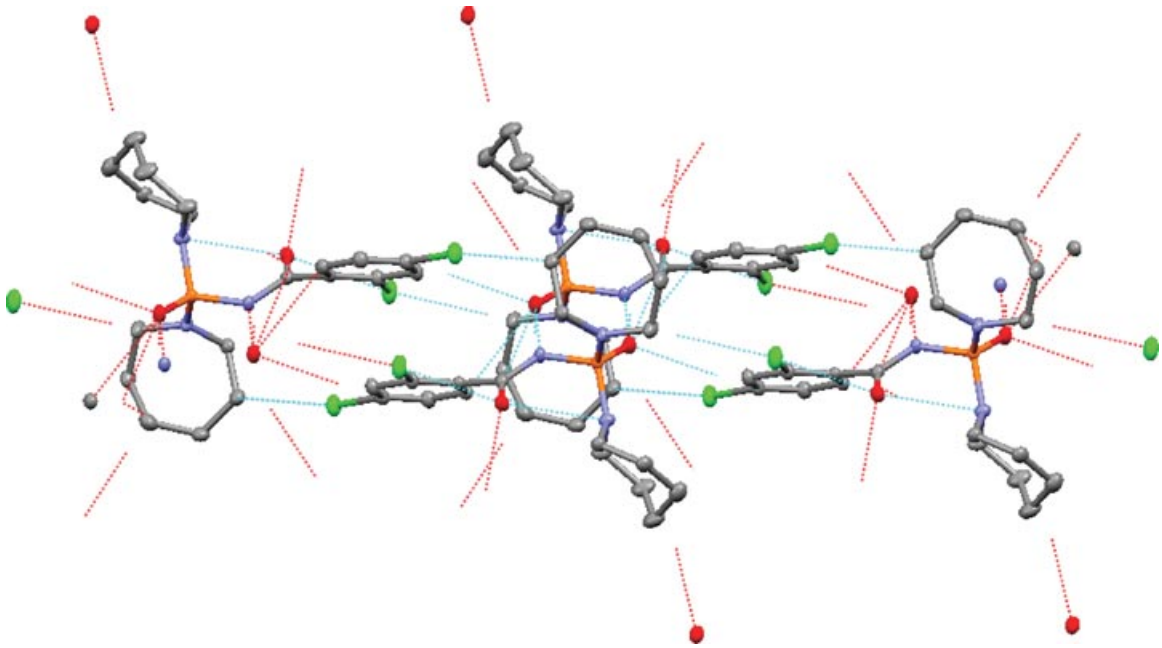


FIGURE 6 A two-dimensional polymeric chain produced by strong and weak hydrogen bonds in the crystalline lattice of compound **4**.

distances equal to 3.030 Å and 3.049 Å, respectively. Such an intramolecular electrostatic interaction is detected between O(2) of C=O group and *ortho* Cl(1) atoms, with O-Cl distances of about 3.0 Å in **3, 6, 6a**, and **10**.

A comparison of structure **3** with its analogues $XP(O)(NC_5H_{10})_2$, where X = 4-$ClC_6H_4C(O)NH$ (**12**) [26], and $C_6H_5C(O)NH$ (**19**) [41] indicates that with an increase in the number of Cl atoms on the ring, the P=O bond becomes longer whereas the C=O bond length becomes shorter. Moreover, compound **19** indicated four conformers in the solid state but molecules **12** and **3** do not exhibit this feature.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structures **3, 4, 6**, **6a**, and **10** have been deposited with Cambridge Crystallographic Data Center (CCDC) as supplementary publication numbers: CCDC

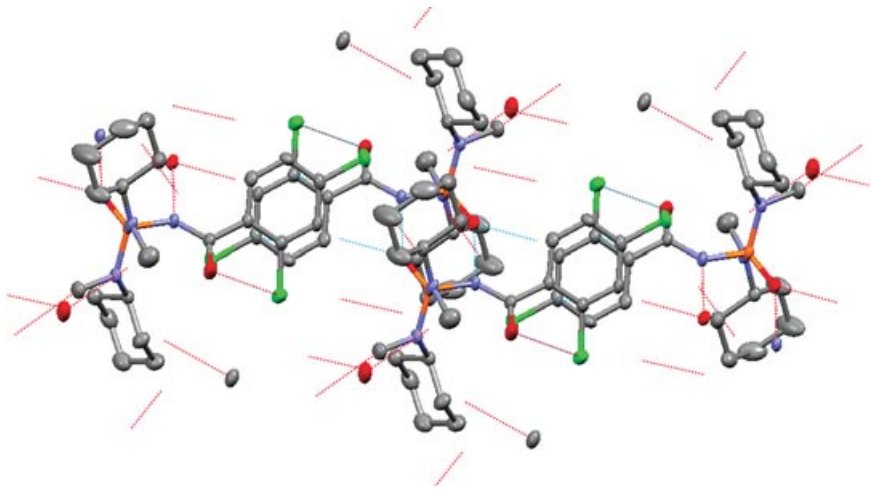


FIGURE 7 A two-dimensional polymeric chain produced by strong hydrogen bonds and electrostatic interactions in the crystalline lattice of compound **10**.

TABLE 7 Hydrogen Bonds for Compounds **3**,**4, 6, 6a**, and **10** (Å, °)

Compound	*(D—H···A)*	*d(D—H)*	*d(H···A)*	*d(D···A)*	*∠DHA*
3	N(1)—H(1N)···O(1) #1	0.86(2)	1.93(2)	2.788(2)	175(1)
4	N(3)—H(3N)···O(1) #2	0.91	1.89	2.781(2)	167
6	N(1)—H(1N)···O(2) #2	0.95	1.85	2.795(3)	171
6a	N(1)—H(1N)···O(2) #3	0.82(3)	1.94(3)	2.755(3)	171(2)
10	N(1)—H(1N)···O(1) #4	1.00(2)	1.831(19)	2.826(4)	176(3)

Symmetry transformations used to generate equivalent atoms: #1, $-x+1, -y+2, -z+1$; #2, $-x, -y+1, -z$; #3, $-x+1, -y, -z$; #4, $-x+1, -y+1, -z+1$.

727882 ($C_{17}H_{24}Cl_2N_3O_2P$), CCDC 709119 ($C_{19}H_{28}Cl_2N_3O_2P$), CCDC 727880 ($C_{15}H_{20}Cl_2N_3O_4P$), CCDC 727881 ($C_{15}H_{20}Cl_2N_3O_4P$), and CCDC 709120 ($C_{21}H_{32}Cl_2N_3O_2P$). Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; or www: http://www.ccdc.cam.ac.uk).

REFERENCES

[1] Ashani, Y.; Bhattacharjee, A. K.; Leader, H.; Saxena, A.; Doctor, B. P. Biochem Pharm 2003, 66, 191.

[2] Wong, L.; Radié, Z.; Brüggenmann, R. J. M.; Hosea, N.; Berman, H. A.; Taylor, P. Biochemistry 2000, 39, 5750.

[3] Li, Z.; Han, J.; Jiang, Y.; Browne, P.; Knox, R. J.; Hu, L. Bioinorg Med Chem 2003, 11, 4171.

[4] Zou, X. J.; Jin, G. Y.; Zhang, Z. X. J Agric Food Chem 2002, 50, 1451.

[5] Akgür, S.A.; Öztürk, P.; Solak, I.; Moral, A. R.; Ege, B.; Forensic Sci Int 2003, 133, 136.

[6] Berlicki, L.; Kafarski, P. Pestic Biochem Phys 2002, 73, 94.

[7] Pardio, V. T.; Ibarra, N.; Rodriguez, M. A. J Agric Food Chem 2001, 49, 6057.

[8] Denmark, S. E.; Fu, J. J Am Chem Soc 2003, 125, 2208.

[9] (a) Gubina, K. E.; Shatrava, J. A.; Amirkhanov, V. A.; Ovchynnikov, V. A.; Amirkhanov, V. M. Polyhedron 2000, 19, 2203. (b) Znovjyak, K. O.; Moroz, O. V.; Ovchynnikov, V. A.; Sliva, T. Y.; Shishkina, S. V.; Amirkhanov, V. M. Polyhedron 2009, 28, 3731.

[10] Silvestru, C.; Rösler, R.; Silvestru, A.; Drake, J. E. J Organomet Chem 2002, 642, 71.

[11] Garciay Garcia, P.; Cruz-Almanza, R.; Toscano, R.-A.; Cea-Olivares, R. J Organomet Chem 2000, 598, 160.

[12] Gholivand, K.; Védova, C. O. D.; Erben, M. F.; Mahzouni, H. R.; Shariatinia, Z.; Amiri, S. J Mol Struct 2008, 874, 178.

[13] Domínguez, Z. J.; Cortez, M. T.; Gordillo, B. Tetrahedron 2001, 57, 9799.

[14] Tecilla, P.; Chang, S.-K.; Hamilton, A. D. J Am Chem Soc 1990, 112, 9586.

[15] Moreno, G. E.; Quintero, L.; Bernés, S.; de Parrodi, C. A. Tetrahedron Lett 2004, 45, 4245.

[16] Denmark, S. E.; Su, X.; Nishigaichi, Y.; Coe, D. M.; Wong, K.-T.; Winter, S. B. D.; Choi, J. Y. J Org Chem 1999, 64, 1958.

[17] Ryu, S.; Jackson, J. A.; Thompson, C. M. J Org Chem 1991, 56, 4999.

[18] Necas, M.; Foreman, M. R. St. J.; Dastych, D.; Novosad, J. Inorg Chem Commun 2001, 4, 36.

[19] Gubina, K. E.; Amirkhanov, V. M. Z Naturforsch 2000, 55b, 1015.

[20] Gubina, K. E.; Ovchynnikov, V. A.; Amirkhanov, V. M.; Silva, T. Y.; Skopenko, V. V.; Glowiak, T.; Kozlowski, H. Z Naturforsch 1999, 54b, 1357.

[21] (a) Amirkhanov, V. M.; Ovchynnikov, V. A.; Glowiak, T.; Kozlowski, H. Z Naturforsch 1997, 52b, 1331. (b) Znovjyak, K. O.; Ovchynnikov, V. A.; Sliva, T. Y.; Shishkinab, S. V.; Amirkhanov, V. M. Acta Crystallogr 2009, E65, o2812.

[22] (a) Gholivand, K.; Pourayoubi, M.; Mostaanzadeh, H. Anal Sci 2004, 20, 51; (b) Pourayoubi, M.; Sabbaghi, F. J Chem Crystallogr 2009, 39, 874.

[23] Gholivand, K.; Pourayoubi, M.; Shariatinia, Z.; Mostaanzadeh, H. Polyhedron 2005, 24, 655.

[24] Narula, P. M.; Day, C. S.; Powers, B. A.; Odian, M. A.; Lachgar, A.; Pennington, W. T.; Noftle, R. E. Polyhedron 1999, 18, 1751.

[25] Gholivand, K.; Mostaanzadeh, H.; Koval, T.; Dusek, M.; Erbenc, M. F.; Védova, C. O. D. Acta Crystallogr 2009, B65, 502.

[26] Gholivand, K.; Mojahed, F.; Madani Alizadehgan, A.; Bijanzadeh, H. R. Z Anorg Allg Chem 2006, 632, 1570.

[27] Gholivand, K.; Madani Alizadehgan, A.; Mojahed, F.; Anaraki Firooz, A. S Afr J Chem 2007, 60, 91.

[28] Gholivand, K.; Madani Alizadehgan, A.; Mojahed, F.; Soleimani, P. Polyhedron 2008, 27, 1639.

[29] Gholivand, K.; Madani Alizadehgan, A.; Mojahed, F. Polish J Chem 2007, 81, 393.

[30] Rollinger, J. M.; Gstrein, E. M.; Burger, A. Eur J Pharm Biopharm 2002, 53, 75.

[31] Byrn, S.; Pfeiffer, R. R.; Ganey, M.; Hoiberg, C.; Poochikian, G. Pharm Res 1995, 12, 945.

[32] Barendt, J. M.; Bent, E. G.; Haltiwanger, R. C.; Squier, C. A.; Norman, A. D. Inorg Chem 1989, 28, 4425.

[33] (a) Bruker, SMART. Bruker Molecular Analysis Research Tool, version 5.059; Bruker AXS: Madison, WI, 1998; (b) Bruker, Programs APEX II, version 2.0-1; SAINT, version 7.23A.

[34] SHELXTL, version 6.1. Bruker. AXS Inc., Madison, WI, 2005.

[35] (a) Sheldrick, G. M. SHELXTL version 5.10, Structure Determination Software Suit, Bruker AXS: Madison, WI, 1998; (b) Sheldrick, G. M. SADABS, version 2004/1; XPREP, version 2005/2. Bruker/

Siemens Avea Detector, Absorption Correction Program, Bruker AXS, Madison, WI, 1998.
[36] Kitamura, M.; Nakamura, K. J Cryst Growth 2002, 236, 676.
[37] Kitamura, M.; Ishizu, T. J Cryst Growth 1998, 192, 225.
[38] Barfield, M.; Chakrabarti, B. Chem Rev 1969, 69, 757.
[39] Corbridge, D. E. C. Phosphorus, an Outline of Its Chemistry, Biochemistry and Technology, 5th ed.; Elsevier: the Netherlands, 1995, pp. 55–57.
[40] Gilheany, D. G. Chem Rev 1994, 94, 1339.
[41] Gholivand, K.; Vedova, C. O. D.; Anaraki Firooz, A.; Madani Alizadehgan, A.; Michelini, M. C.; Pis Diez, R. J Mol Struct 2005, 750, 64.
[42] Gholivand, K.; Mostaanzadeh, H.; Shariatinia, Z.; Oroujzadeh, N. Main Group Chem 2006, 5, 95.
[43] Gholivand, K.; Hosseini, Z.; Pourayoubi, M.; Shariatinia, Z. Z Anorg Allg Chem 2005, 631, 3074.
[44] Gholivand, K.; Shariatinia, Z. Struct Chem 2007, 18, 95.