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N-2,4-Dichlorobenzoyl phosphoric triamides: Synthesis, spectroscopic and X-ray crystallography studies

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Abstract. New phosphoric triamides **1–9** 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, IR spectroscopy and elemental analysis. Surprisingly, the ^{1}H NMR spectrum of **2** indicated long range ^{6}J (P, H) coupling constant = 1·3, 1·4 Hz and those of molecules **3**, **4**, **6–8** display long-range ^{4}J (H, H) coupling constants (1·8–1·9 Hz) for the coupling of aromatic protons in 2,4-dichlorophenyl rings. ^{1}H NMR spectra indicated ^{3}J (PNCH) for enantiotopic and diastereotopic benzylic CH_2 protons in compounds **7** and **8**. The spectroscopic data of newly synthesized compounds were compared with those related *N*-benzoyl derivatives. The structures of compounds **5**, **8** and **10** (2,4-Cl_2-$C_6H_3C(O)NHP(O)[NCH_2CH(CH_3)_2]_2$) have been determined by X-ray crystallography. The structures form centrosymmetric dimers through intermolecular strong –P=O…H–N-hydrogen bonds. The dimers connect to each other via rather strong and weak C–H…O plus weak C–H…Cl H-bonds to produce a 1-D network for **5** while 3-D polymeric chains for **8** and **10**.

Keywords. Phosphoric triamides; NMR; long range coupling; X-ray crystallography; hydrogen bonds.

1. Introduction

Nowadays, there is a growing interest to research on phosphoramidates chemistry that is because of the valuable applications of these derivatives. Specially, pharmacologists try to find novel and efficient drugs from this class of compounds similar to cyclophosphamide.[1–5] Moreover, they have important applications as insecticides and pesticides[6–9] and efficient ligands in coordination chemistry.[10–13] The synthesis,[14–17] theoretical[18,19] and structural studies[20–24] have been performed on these compounds. The structures of several phosphoramidates have already been determined by X-ray crystallography.[20–27,28–31] *N*-benzoylphosphoric triamides are one such significant category of phosphoramidates derivatives. In fact, the existence of –C(O)NHP(O)– skeleton as peptide group in these molecules cause them biologically active urease inhibitors.[32–34] Recently, it has been reported that phosphorus triester derivatives of 3-azido-3-deoxythymidine (AZT) bearing amino acid moieties revealed enhanced anti-HIV activity.[35]

Hydrogen bonding is an important topic of intense research in both chemistry and biology.[36,37] Swamy *et al* investigated very strong C–H…O, N–H…O and O–H…O hydrogen bonds in a cyclic phosphate.[38,39] The formation of centrosymmetric dimers via strong and weak N–H…O hydrogen bonds were studied.[40,41] In the present paper, following on our previous studies, new *N*-2,4-dichorobenzoyl phosphoric triamides have been prepared and characterized by ^{1}H, ^{13}C, ^{31}P NMR, IR spectroscopy. Also, the structures of compounds **5**, **8** and **10** (2,4-Cl_2-$C_6H_3C(O)NHP(O)[NCH_2CH(CH_3)_2]_2$)[42] have been determined by X-ray crystallography and their hydrogen bonded networks have been analysed. The spectroscopic data of newly synthesized compounds have been compared with those related *N*-benzoyl analogues.

2. Experimental

2.1 *X-ray measurements*

X-ray data of compound **5** were collected on a X-area 1.31[43a] and those of compounds **8** and **10** on

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a Bruker SMART 1000 CCD[43b] single crystal diffractometer with graphite monochromated MoKα radiation (λ = 0·71073 Å). The structures were refined with SHELXL-97[44] by full matrix least squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map. While the shape of crystal determined optically in **5**, routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program for structures **8** and **10**.[45]

2.2 *Spectroscopic measurements*

^{1}H, ^{13}C and ^{31}P spectra were recorded on a Bruker Avance DRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts were determined relative to internal Me_4Si, ^{31}P chemical shifts relative to 85% H_3PO_4 as external standards, respectively. The field strengths to acquisition of ^{1}H, ^{13}C and ^{31}P NMR spectra were 500.13, 125.77, and 202.46 MHz, respectively. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

2.3 *Synthesis*

2.3a *N-2,4-dichlorobenzoyl phosphoramidic dichloride* (**1**): Phosphorus pentachloride and 2,4-dichlorobenzamide in 1 : 1 molar ratio were refluxed in CCl_4 for 8 h, and then the resulting solution allowed to cool to the room temperature. Formic acid was syringed drop-wise into the stirring solution in 20 min and was stirred for 6h to yield the 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 (*s*, C=O), 1582 (*s*), 1428 (*s*), 1276 (*m*), 1249 (*m*), 1227 (*s*, P=O), 1102 (*m*), 1043 (*m*), 896 (*s*), 832 (*m*), 781 (*m*), 756 (*m*), 678 (*m*), 586 (*m*), 516 (*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, 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). ^{31}P NMR (202·46 MHz; $CDCl_3$; 85% H_3PO_4): δ 5·99 (*m*).

2.3b *N-2,4-dichlorobenzoyl-dihydroxy phosphoramide* (**2**): A solution of 1 mmol *N*-2,4-dichlorobenzoyl phosphoramidic dichloride (**1**) in distilled water was stirred for 6 h. The precipitate was filtered and dried. Yield: 96%; m.p. = 139·6°C. Anal. Calcd. for $C_7H_6Cl_2NO_4P$ (%): C, 31·11; H, 2·22; N, 5·18. Found: C, 31·10; H, 2·23; N, 5·18. IR (KBr, cm^{-1}): 3170 (*m*, CH), 2835 (*m*), 1697 (*s*, C=O), 1574 (*m*), 1425 (*s*), 1278 (*m*), 1251 (*m*), 1222 (*s*, P=O), 1098 (*s*), 1040 (*m*), 958 (*m*), 892 (*m*), 778 (*m*), 676 (*m*), 583 (*m*), 512 (*m*). ^{1}H NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 7·42 (*d*, ^3J (H, H) = 8·2 Hz, 1H), 7·47 (*dd*, ^3J (H, H) = 8·3 Hz, ^6J (P, H) = 1·3 Hz, 1H, Ar-H), 7·64 (*d*, ^6J (P, H) = 1·4 Hz, 1H, Ar-H), 9·64 (*d*, ^2J (PNH) = 9·5 Hz, 1H, NH), 11·93 (*s*, 2H, OH). ^{1}H{^{31}P} NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 7·42 (*d*, ^3J (H, H) = 8·2 Hz, 1H), 7·47 (*d*, ^3J (H, H) = 8·3 Hz, 1H, Ar-H), 7·64 (*s*, 1H, Ar-H), 9·64 (*s*, 1H, NH), 11·93 (*s*, 2H, OH). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 127·09 (*s*), 129·04 (*s*), 130·08 (*s*), 130·97 (*s*), 134·65 (*s*), 135·17 (*d*, ^3J(P,C) = 10·3 Hz, C_{ipso}), 166·75 (*s*, C=O). ^{31}P{^{1}H} NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ –6·10 (*s*).

2.4 *General procedure for the synthesis of compounds* **3–9**

To a solution of 10 mmol *N*-2,4-dichlorobenzoyl phosphoramidic dichloride (**1**) in dry acetonitrile at –5°C, 40 mmol of corresponding amine was added drop-wise 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.

2.4a *N-2,4-Dichlorobenzoyl-N′,N″-diallyl phosphoric triamide* (**3**): Yield: 73%; m.p. = 159·1°C. Anal. Calcd. for $C_{13}H_{16}Cl_2N_3O_2P$ (%): C, 44·83; H, 5·00; N, 12·07. Found: C, 44·81; H, 5·01; N, 12·06. IR (KBr, cm^{-1}): 3235 (*s*, NH), 2885 (*w*), 1648 (*s*, C=O), 1577 (*m*), 1434 (*s*), 1276 (*m*), 1236 (*m*), 1196 (*s*, P=O), 1130 (*m*), 1096 (*m*), 1038 (*m*), 985 (*m*), 918 (*m*), 887 (*m*), 860 (*m*), 767 (*m*), 567 (*w*), 495 (*m*), 430 (*m*). ^{1}H NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 3·48 (*m*, 4H, CH_2), 4·58 (*m*, 2H, NH_{amine}), 5·01 (*dd*, ^2J(H,H) = 1·7 Hz, ^3J(H,H) = 10·3 Hz, 2H), 5·21 (*m*, 2H), 5·84 (*m*, 2H), 7·48 (*m*, 2H), 7·66 (*d*, ^4J(H,H) = 1·9 Hz, 1H, Ar-H), 9·50 (*d*, ^2J(PNH) = 7·2 Hz, 1H, NH_{amide}). ^{13}C NMR (125·76

MHz, d_6-DMSO, 25°C, TMS): δ 43·37 (*s*, CH_2), 115·35 (*s*, CH_2), 128·04 (*s*), 129·98 (*s*), 131·13 (*s*), 131·76 (*s*), 135·60 (*s*), 136·21 (*d*, ^3J (P, C) = 8·7 Hz, C_{ipso}), 138·43 (*d*, ^3J (P, C) = 6·2 Hz, CH), 168·03 (*s*, C=O). $^{31}P\{^1H\}$ NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 8·34 (*s*).

2.4b *N-2,4-Dichlorobenzoyl-N',N''-diisopropyl phosphoric triamide* (**4**): Yield: 74%; m.p. = 144·9°C. Anal. Calcd. for $C_{13}H_{20}Cl_2N_3O_2P$ (%): C, 44·32; H, 5·68; N, 11·93. Found: C, 44·30; H, 5·67; N, 11·91. IR (KBr, cm^{-1}): 3360 (*m*, NH), 3090 (*m*), 2975 (*m*), 1656 (*s*, C=O), 1581 (*m*), 1475 (*m*), 1436 (*s*), 1286 (*m*), 1214 (*s*, P=O), 1132 (*m*), 1106 (*m*), 1039 (*m*), 1016 (*m*), 898 (*m*), 847 (*w*), 769 (*m*), 691 (*w*), 572 (*m*), 538 (*m*), 464 (*w*). ^1H NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 1·08 (*m*, 12H, CH_3), 3·29–3·35 (*m*, 2H, CH), 4·14 (*dd*, ^3J (H, H) = 9·1, ^2J(PNH) = 9·6 Hz, 2H, NH_{amine}), 7·42 (*d*, ^3J(H, H) = 8.2 Hz, 1H, Ar-H), 7·47 (*dd*, ^3J (H, H) = 8·2, ^4J (H, H) = 1·9 Hz, 1H, Ar-H), 7·64 (*d*, ^4J (H, H) = 1·9 Hz, 1H, Ar-H), 9·41 (*s*, 1H, NH_{amide}). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 24·93 (*d*, ^3J (P, C)$_{Aliphatic}$ = 5·0 Hz, CH_3), 25·31 (*d*, ^3J (P, C)$_{Aliphatic}$ = 6·0 Hz, CH_3), 42·22 (*s*, CH), 127·15 (*s*), 128·79 (*s*), 129·10 (*s*), 130·12 (*s*), 130·85 (*s*), 134·61 (*s*), 135·42 (*d*, ^3J (P, C) = 8·6 Hz, C_{ipso}), 166·97 (*s*, C=O). $^{31}P\{^1H\}$ NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 4·28 (*s*).

2.4c *N-2,4-Dichlorobenzoyl-N',N''-di-tert-butyl phosphoric triamide* (**5**): Yield: 95%; m.p. = 175·3°C. Anal. Calcd. for $C_{15}H_{24}Cl_2N_3O_2P$ (%): C, 47·37; H, 6·32; N, 11·05. Found: C, 47·35; H, 6·33; N, 11·04. IR (KBr, cm^{-1}): 3365 (*m*), 3105 (*m*), 2970 (*m*), 1655 (*s*, C=O), 1583 (*m*), 1479 (*m*), 1430 (*s*), 1385 (*m*), 1286 (*m*), 1251 (*m*), 1219 (*s*, P=O), 1105 (*m*), 1041 (*m*), 1009 (*m*), 890 (*m*), 861 (*m*), 772 (*m*), 749(*m*), 684 (*w*), 588 (*w*), 539 (*w*). ^1H NMR (500.13 MHz, d_6-DMSO, 25°C, TMS): δ 1·24 (*s*, 18H, CH_3), 4·01 (*d*, ^2J(PNH) = 7·6 Hz, 2H, NH_{amine}), 7·47 (*m*, 2H, Ar-H), 7·63 (*s*, 1H, Ar-H), 9·58 (*s*, 1H, NH_{amide}). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 31·26 (*d*, ^3J(P,C)$_{Aliphatic}$ = 4·8 Hz, CH_3), 50·41 (*s*), 126·99 (*s*), 129·11 (*s*), 130·36 (*s*), 131·04 (*s*), 134·58 (*s*), 135·27 (*d*, ^3J (P, C) = 6·9 Hz, C_{ipso}), 166·93 (*s*, C=O). $^{31}P\{^1H\}$ NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 0·85 (*s*).

2.4d *N-2,4-Dichlorobenzoyl-N',N''-difurfuryl phosphoric triamide* (**6**): Yield: 89%; m.p. = 133·7°C. Anal. Calcd. for $C_{17}H_{16}Cl_2N_3O_4P$ (%): C, 47·66; H, 3·74; N, 9·81. Found: C, 47·64; H, 3·73; N, 9·82. IR (KBr, cm^{-1}): 3245 (*s*, NH), 3140 (*m*), 2895 (*m*), 1662 (*s*, C=O), 1575 (*m*), 1466 (*m*), 1421 (*s*), 1273 (*m*), 1202 (*s*, P=O), 1139 (*m*), 1094 (*m*), 1065 (*m*), 1006 (*m*), 919 (*m*), 880 (*m*), 768 (*m*), 734 (*m*), 687 (*w*), 593 (*w*), 460 (*m*). ^1H NMR (500.13 MHz, d_6-DMSO, 25°C, TMS): δ 4·02 (*m*, 4H, CH_2), 4·98 (*m*, 2H, NH_{amine}), 6·26–6·36 (*m*, 4H), 7·41 (*d*, ^3J(H,H) = 8·3 Hz, 1H), 7·47 (*dd*, ^4J (H,H) = 1·9 Hz, ^3J (H, H) = 8·2 Hz, 1H), 7·52 (*d*, ^3J (H, H) = 0·8 Hz, 2H), 7·64 (*d*, ^4J (H, H) = 1·9 Hz, 1H), 9·57 (*d*, ^2J (PNH) = 7·9 Hz, 1H, NH_{amide}). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 37·01 (*s*,CH_2), 106·25 (*s*), 110·26 (*s*), 127·00 (*s*), 129·01 (*s*), 130·29 (*s*), 130·86 (*s*), 134·72 (*s*), 135·02 (*d*, ^3J (P, C) = 8·8 Hz, C_{ipso}), 141·69 (*s*), 154·02 (*d*, ^3J (P, C) = 6·9 Hz), 167·04 (*s*, C=O). $^{31}P\{^1H\}$ NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 7·42 (*s*).

2.4e *N-2,4-Dichlorobenzoyl-N',N''-dibenzyl phosphoric triamide* (**7**): Yield: 87%; m.p. = 175·5°C. Anal. Calcd. for $C_{21}H_{20}Cl_2N_3O_2P$ (%): C, 56·25; H, 4·46; N, 9·37. Found: C, 56·24; H, 4·45; N, 9·36. IR (KBr, cm^{-1}): 3280 (*s*, NH), 3135 (*m*), 1669 (*s*, C=O), 1586 (*m*), 1474 (*m*), 1432 (*s*), 1183 (*s*, P=O), 1125 (*m*), 1100 (*m*), 1026 (*m*), 995 (*w*), 881 (*m*), 832 (*w*), 766 (*m*), 737 (*m*), 690 (*m*), 603 (*w*). ^1H NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 4·08 (*dd*, ^3J (H, H) = 7·3, ^3J (PNCH) = 11·7 Hz, 4H, CH_2), 5·05 (*td*, ^3J (H, H) = 7·1 Hz, ^2J (PNH) = 7·2 Hz, 2H, NH_{amine}), 7·17–7·38 (*m*, 11H, Ar-H), 7·45 (*dd*, ^3J (H, H) = 8·3 Hz, ^4J (H, H) = 1·9 Hz, 1H), 7·64 (*d*, ^4J (H, H) = 1·9 Hz, 1H), 9·59. (*s*, 1H, NH_{amide}). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 43·72 (*s*, CH_2), 126·49 (*s*), 127·02 (*s*), 127·22 (*s*), 127·98 (*s*), 129·04 (*s*), 130·25 (*s*), 130·88 (*s*), 134·69 (*s*), 135·25 (*d*, ^3J (P, C) = 8·9 Hz, C_{ipso}), 141·00 (*d*, ^3J (P, C) = 5·8 Hz), 167·14 (*s*, C=O). $^{31}P\{^1H\}$ NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 7·36 (*s*).

2.4f *N-2,4-Dichlorobenzoyl-N',N''-bis (N-methylbenzyl) phosphoric triamide* (**8**): Yield: 91%; m.p. = 169·3°C. Anal. Calcd. for $C_{23}H_{24}Cl_2N_3O_2P$ (%): C, 52·94; H, 5·04; N, 8·82. Found: C, 52·95; H, 5·02; N, 8·84. IR (KBr, cm^{-1}): 3015 (*s*), 2835 (*s*), 1676 (*s*, C=O), 1573 (*m*, ν_{ring}), 1440 (*s*), 1340 (*m*), 1282 (*m*), 1212 (*s*), 1180 (*s*, P=O), 1127 (*s*), 1100 (*m*), 1045 (*m*), 1011 (*s*), 947 (*s*), 867 (*m*), 814

(*m*),776 (*m*), 728 (*m*), 532 (*m*), 502 (*m*), 441 (*m*). ^{1}H NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 2·55 (*d*, ^{3}J (P, H) = 10·1 Hz, 6H, CH_3), 4·16 (*dd*, ^{2}J (H, H) = 15·1, ^{3}J (P, H) = 8·7 Hz, 2H), 4·24 (*dd*, ^{2}J (H, H) = 15·1, ^{3}J (P, H) = 9·3 Hz, 2H), 7·27 (*m*, 2H), 7·35 (*m*, 4H), 7·42 (*m*, 4H), 7·46 (*m*, 1H), 7·51 (*dd*, ^{3}J (H, H) = 8·2, ^{4}J (H, H) = 1·8 Hz, 1H), 7·71 (*d*, ^{4}J (H, H) = 1·8 Hz, 1H), 9·80 (*s*, 1H, NH_{amide}). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 33·33 (*d*, ^{2}J (P, C) = 4·2 Hz, CH_3), 52·02 (*d*, ^{2}J (P, C) = 4·4 Hz, CH_2), 127·06 (*s*), 127·32 (*s*), 127·99 (*s*), 128·31 (*s*), 129·16 (*s*), 130·09 (*s*), 130·85 (*s*), 134·92 (*s*), 135·39 (*s*), 138·21 (*d*, ^{3}J (P, C) = 4·4 Hz), 168·61 (*s*, C=O). ^{31}P{^{1}H} NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 12·90 (*s*).

2.4g *N-2,4-Dichlorobenzoyl-N′,N″-bis (α-methylbenzyl) phosphoric triamide* (**9**): Yield: 95%; m.p. = 208.9°C. Anal. Calcd. for $C_{23}H_{24}Cl_2N_3O_2P$ (%): C, 57·98; H, 5·04; N, 8·82. Found: C, 57·96; H, 5·05; N, 8·83. IR (KBr, cm^{-1}): 3255 (*s*, NH), 2955 (*m*), 1664 (*s*, C=O), 1586 (*m*), 1473 (*m*), 1424 (*s*), 1280 (*m*), 1202 (*s*, P=O), 1103 (*m*), 1041 (*m*), 973 (*m*), 891 (*m*), 768 (*m*), 694 (*m*). ^{1}H NMR (500·13 MHz, d_6-DMSO, 25°C, TMS): δ 1·37 (*d*, ^{3}J (H, H) = 6·8 Hz, 3H, CH_3), 1·39 (*d*, ^{3}J (H, H) = 6·8 Hz, 3H, CH_3), 4·38 (*m*, 2H), 4·80 (*dd*, ^{2}J (PNH) = ^{3}J (H, H) = 10·2 Hz, 1H, NH_{amine}), 4·92 (*dd*, ^{2}J (PNH) = ^{3}J(H,H) = 10.2 Hz, 1H, NH_{amine}), 7·10–7·61 (*m*, 13H, Ar-H), 9·44 (*d*, ^{2}J(PNH) = 7·9 Hz, 1H, NH_{amide}). ^{13}C NMR (125·76 MHz, d_6-DMSO, 25°C, TMS): δ 25·14 (*d*, ^{3}J (P, C) = 5·0 Hz, CH_3), 25·51 (*d*, ^{3}J (P, C) = 6·3 Hz, CH_3), 46·68 (*s*), 49·88 (*s*), 125·91 (*s*), 126·00 (*s*), 126·24 (*s*), 126·29 (*s*), 126·90 (*s*), 127·92 (*s*), 127·94 (*s*), 129·00 (*s*), 130·25 (*s*), 130·88 (*s*), 134·65 (*s*), 135·08 (*d*, ^{3}J (P, C) = 8·8 Hz), 146·01 (*d*, ^{3}J (P, C) = 3.7 Hz), 146·22 (*d*, ^{3}J (P, C) = 5.4 Hz), 166·95 (*s*, C=O). ^{31}P{^{1}H} NMR (202·46 MHz, d_6-DMSO, 25°C, H_3PO_4 external): δ 3·99 (*s*).

3. Results and discussion

3.1 *Spectroscopic study*

In this work, several new phosphoric triamides **1–9** were prepared from the reaction of *N*-2,4-$Cl_2C_6H_3C(O)NHP(O)Cl_2$ (**1**) with H_2O or various amines (scheme 1). Some spectroscopic data of the new compounds and their analogues are summarized in table 1. It is interesting that ^{31}P NMR chemical shift, δ (^{31}P), in compound **2** with two OH groups is the most upfield while in other compounds containing two chlorine atoms or amino moieties, the δ (^{31}P) greatly shifts to down field. In compounds **3–5** with aliphatic amino groups, δ (^{31}P) decreases from **3** to **5** and it is nearly 8 and 4 times greater in **3** and **4** than in **5**, respectively. The ^{31}P NMR chemical shifts in **6** and **7** are close to each other. Comparison of compounds **7–9** containing benzylic substituents indicate that replacement of $CH_2C_6H_5$ groups in **7** by $N(CH_3)(C_6H_5)$ and $N\text{-}CH(CH_3)(C_6H_5)$ moieties in **8** and **9** cause a highly deshielded and shielded phosphorus atom, respectively. This means the effects of these two substituents are opposite to each other. Comparison of δ (^{31}P) values for compounds **4–10** (containing 2,4-dichlorobenzoyl moiety) and their analogues **13–19** (containing benzoyl moiety) reveal that the δ (^{31}P) values are at down fields for **13–19**. It seems that the presence of two Cl atoms on the phenyl ring in molecules **4–10** cause more shielded phosphorus atoms by electron donation via resonance effect.

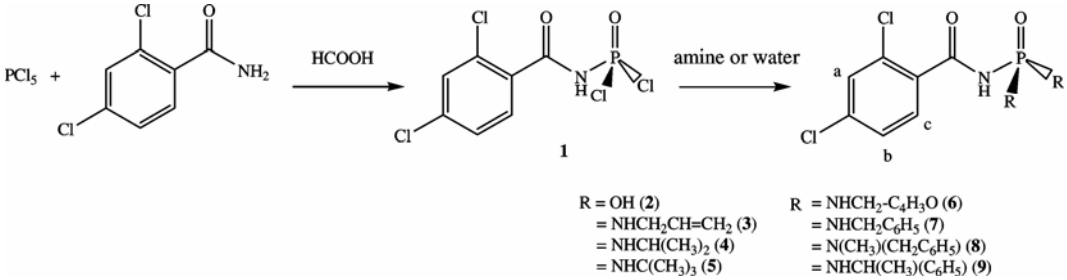
Interestingly, the ^{1}H NMR spectra of compounds **2** and **10** indicated long range ^{6}J (P, H) coupling constants = 1·3, 1·4 Hz and 1·7, 1·7 Hz, respectively, for the splitting of meta protons (a, b protons shown in scheme 1) with phosphorus atom. Figure 1 indicates the ^{1}H- and ^{1}H{^{31}P} NMR spectra of compound **2**. Also, the spectra of molecules **1**, **3**, **4**, **6–8** display long-range ^{4}J (H, H) coupling constants (1·8–1·9 Hz) for the coupling of aromatic protons in 2,4-dichlorophenyl rings. This coupling was observed neither for compounds **11–19** nor for our previously reported phosphoric triamides.[24,25,28–31,43–45] Typically, ^{4}J (H, H) coupling constants for the phenyl ring are in the range of 1–3 Hz and particular values seem to depend as much on the pattern of substitution as the nature of the substituent.[46]

The ^{1}H NMR spectrum of compound **3** exhibited ^{3}J (H, H)$_{cis}$ = 10·3 Hz and ^{3}J (H, H)$_{trans}$ = 17·2 Hz for the coupling of terminal CH_2 protons of $-CH=CH_2$ with CH proton. ^{3}J (PNCH) was observed in compounds **7** and **8** for the splitting of benzylic CH_2 and CH_3 protons with phosphorus atom. The unequal diastereotopic CH_2 protons in **8** caused two different ^{3}J (PNCH) values while they are identical in **7**. This constant similar to ^{2}J (P, C)$_{aliphatic}$ is greater for CH_3 group than for CH_2 in molecule **8** and its analogue **17**. The ^{1}H- and ^{13}C NMR spectra of compound **9** and its analogue **18** indicated two series of signals

Table 1. Some spectroscopic data of compounds **1–19**.

Compound*	No.	δ (^{31}P) (ppm)	^{2}J (PNH) (Hz)	^{3}J (PNCH) (Hz)	^{4}J (H,H) (Hz)	^{6}J (P, 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.
$R^1P(O)Cl_2$	**1**	5·99	–	–	1·9	–	–	–	10·7	1227	1707	**
$R^1P(O)(OH)_2$	**2**	–6·10	9·5	–	–	1·4 (H_a), 1·3 (H_b)	–	–	10·3	1222	1697	**
$R^1P(O)(NHCH_2CH{=}CH_2)_2$	**3**	8·34	7·2 (amide)		1·9	–	–	6·2	8·7	1196	1648	**
$R^1P(O)[NHCH(CH_3)_2]_2$	**4**	4·28	9·6 (amine)		1·9	–	–	5·0, 6·0	8·6	1210	1648	**
$R^1P(O)[NH\text{-}C(CH_3)_3]_2$	**5**	0·85	7·6 (amine)		–	–	–	4·8	6·9	1219	1655	**
$R^1P(O)(NHCH_2\text{-}C_4H_3O)_2$	**6**	7·42	7·9 (amide)	–	1·9	–	–	–	6·9 (amine), 8·8 (amide)	1202	1662	**
$R^1P(O)(NHCH_2C_6H_5)_2$	**7**	7·36	7·2 (amine)	11·7 (CH_2)	1·9	–	–	–	5·8 (amine), 8·9 (amide)	1183	1669	**
$R^1P(O)[N(CH_3)(CH_2C_6H_5)]_2$	**8**	12·90	–	10·1 (CH_3), 8·7, 9·3 (CH_2)	1·8	–	4·2 (CH_3), 4·4 (CH_2)	–	4·4 (amine)	1180	1676	**
$R^1P(O)[NHCH(CH_3)(C_6H_5)]_2$	**9**	3·99	7·9 (amine), 10·2 (amide)	–	–	–	–	5·0 (CH_3), 6·3 (CH_3)	3·7, 5·4 (amine), 8·8 (amide)	1202	1664	**
$R^1P(O)[NCH_2CH(CH_3)_2]_2$	**10**	14·19	–	–	–	1·7 (H_a), 1·7 (H_b)	3·0 (CH_2)	3·2 (CH)	–	1185	1684	[42]
$R^2P(O)Cl_2$	**11**	10·52	12·0	–	–	–	–	–	10·1	1226	1683	[49]
$R^3P(O)Cl_2$	**12**	9·29	12·0	–	–	–	–	–	10·0	1221	1682	[49]
$R^3P(O)[NHCH(CH_3)_2]_2$	**13**	8·22	9·1 (amine)	–	–	–	–	4·8, 6·6	7·8	1203	1640	[31]
$R^3P(O)[NH\text{-}C(CH_3)_3]_2$	**14**	4·10, 4·70	6·9, 8·0 (amide)	–	–	–	–	4·8, 4·9	7·7, 8·7	1211, 1234	1634	[50]
$R^3P(O)(NHCH_2\text{-}C_4H_3O)_2$	**15**	8·63	–	11·3 (CH_2)	–	–	–	–	6·8 (amine) 8·3 (amide)	1178	1633	
$R^3P(O)(NHCH_2C_6H_5)_2$	**16**	10·07	5·6 (amide)	–	–	–	–	–	6·5 (amine) 8·3 (amide)	1194	1636	[24]
$R^3P(O)[N(CH_3)(CH_2C_6H_5)]_2$	**17**	16·65	–	10·3(CH_3) 9·3, 9·3 ($CH)_2$	–	–	5·0 (CH_3), 5·3 (CH_2)	–	4·2 (amine) 8·7(amide)	1179	1666	[25]
$R^3P(O)[NHCH(CH_3)(C_6H_5)]_2$	**18**	7·03	6·2 (amide)	–	–	–	–	6·2 (CH_3) 7·8 (CH_3)	3·8, 5·0 (amine) 7·9 (amide)	1193	1638	[51]
$R^3P(O)[NCH_2CH(CH_3)_2]_2$	**19**	15·30	6·1 (amide)	–	–	–	–	–	–	1183	1668	[42]

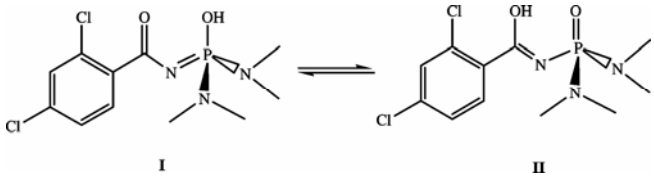
*R^1=2,4-Cl_2-C_6H_3C(O)NH, R^2=4-Cl-C_6H_4C(O)NH, R^3=C_6H_5C(O)NH. **This work.



Scheme 1. The preparation pathway for the synthesis of compounds **1**–**9**.

for the two unequal α-methylbenzyl moieties that is due to the effect of chiral carbon atoms. Similarly, the ^{1}H- and ^{13}C NMR spectra of analogous compounds **10** and **19** demonstrated two series of signals for two different CH_3 groups of diisobutyl substituents which is a result of prochiral CH carbon atoms. The ^{13}C NMR spectrum of compound **4**, containing two isopropyl groups, revealed two different values for the ^{3}J (P, C)$_{aliphatic}$ that could be attributed to the presence of prochiral CH carbon atom.

The ν(P=O) and ν(C=O) in **1** have the greatest values among these molecules. For the molecules **3**–**5**, ν(P=O) value becomes larger from **3** to **5** but ν(C=O) does not change significantly. The ν(P=O) values in compounds **8**, **9** are smaller than in **7** while ν(C=O) exhibits a reverse influence. This could be described by the resonance interaction of P=O and C=O groups as follows in which the superior form in **8** is I while in **9** it is form II.



I II

A comparison of similar compounds **1**, **11** and **12** with formula RC(O)NHP(O)Cl_2, R = 2,4-Cl_2 C_6H_3, 4-ClC_6H_4 and C_6H_5 reveals that with increasing the chlorine atoms on the phenyl ring, both ν(P=O) and ν(C=O) amounts decrease.

3.2 *X-Ray crystallography*

Single crystals of compounds **5**, **8** and **10** (*N*-2,4-$C_6H_3C(O)NHP(O)[NCH_2CH(CH_3)_2]_2$) 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 table 2. Selected bond lengths and angles are presented in table 3 and molecular structures (ORTEP view) are shown in figures 1–3.

In these structures, the phosphoryl and the carbonyl groups indicate anti configurations and the phosphorus atoms have distorted tetrahedral configuration. The bond angles around P(1) atoms in the compounds are in the range of 104·88(7)° to 118·21(7)°. 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 the N_{amide} with the C=O π system that 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). All the P–N bonds are shorter than the typical P–N single bond (1·77 Å[47]). This is probably owing to the electrostatic effects of polar bonds that overlap with P–N sigma bond.[48] The P=O bond lengths in these compounds are larger than the normal P=O bond length (1·45 Å).[47]

The environment of the nitrogen atoms is practically planar. For example, in compound **5** the angles C(7)–N(1)–P(1), C(7)–N(1)–H(1A) and P(1)–N(1)–H(1A) are 124·4(3)°, 117·8° and 117·8°, respectively with an average 120·0°. The sum of surrounding angles around N(2) and N(3) atoms are 352·1° and 358·4°, respectively. Similar results were obtained for the nitrogen atoms of other structure that confirm the sp^2 hybridization for the N atoms, although due to the repulsion and steric interactions, some angles are greater, and others are smaller than 120°. This observation suggests the existence of partial multiple bond character between phosphorus and nitrogen atoms that has always been confirmed by the crystallographic data of our previously reported similar compounds.[24,25,28–31,42,49–51]

These structures contain one amidic hydrogen atom and form centrosymmetric dimers through strong intermolecular –P=O…H–N– hydrogen bonds

Table 2. Crystallographic data for compounds **5**, **8** and **10**.

	5	**8**	**10**
Empirical formula	$C_{15}H_{24}Cl_2N_3O_2P$	$C_{23}H_{24}Cl_2N_3O_2P$	$C_{23}H_{40}Cl_2N_3O_2P$
Formula weight	380·24	476·32	492·45
Temperature (K)	293(2)	120(2)	120(2)
Wavelength (Å)	0·71073	0·71073	0·71073
Crystal system, space group	Triclinic, *P*-1	Tricliniic, *P*-1	Monocliniic, $P2_1/n$
Unit cell dimensions			
a (Å)	10·184(4)	10·5670(11)	13·6999(8)
b (Å)	10·726(5)	11·0083(11)	13·3978(8)
c (Å)	10·674(5)	11·5928(12)	14·3314(9)
α (°)	100·05(3)	68·249(2)	90
β (°)	101·11(3)	71·293(2)	93·340(5)
γ (°)	116·15(3)	68·071(2)	90
V (Å^3)	981·4(7)	1135·6(2)	2626·0(3)
Z, Calculated density (Mg m^{-3})	2, 1·287	2, 1·393	4, 1·246
Absorption coefficient (mm^{-1})	0·423	0·382	0·332
F (000)	400	496	1056
Crystal size (mm)	0·50 × 0·10 × 0·05	0·13 × 0·12 × 0·11	0·25 × 0·25 × 0·15
θ range for data collection (°)	2·03 to 29·21	1·94 to 27·00	2·00 to 29·00
Limiting indices	$-13 \le h \le 13$; $-14 \le k \le 14$; $-14 \le l \le 14$	$-13 \le h \le 13$; $-14 \le k \le 14$; $-14 \le l \le 14$	$-18 \le h \le 18$; $-18 \le k \le 18$; $-19 \le l \le 14$
Reflections collected/unique	9512/4853 [*R*(int) = 0·0426]	10886/4953 [*R*(int) = 0·0181]	23120/6964 [*R*(int) = 0·0339]
Completeness to theta (%)	91·4	99·9	99·7
Absorption correction	Numerical	Semi-empirical from equivalents	Multi-tran
Max. and min. transmission	0·980 and 0·950	0·962 and 0·953	0·959 and 0·926
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	4853/0/216	4953/0/280	6964/0/288
Goodness-of-fit on F^2	1·099	1·022	1·005
Final *R* indices	$R1 = 0·0832$, $wR_2 = 0·1991$	$R_1 = 0·0379$, $wR_2 = 0·0765$	$R_1 = 0·0469$, $wR_2 = 0·1074$
R indices (all data)	$R1 = 0·1270$, $wR_2 = 0·2244$	$R_1 = 0·0458$, $wR_2 = 0·0818$	$R_1 = 0·0677$, $wR_2 = 0·1159$
Largest diff. peak and hole (e.Å^{-3})	0·673 and –0·554	0·450 and –0·324	0·575 and –0·300

(table 4). For example, the P1–O2…H1A–N1 hydrogen bonds produce a centrosymmetric dimer in **5** and this dimer is connected to neighbouring dimers via intermolecular N3–H3…O1, C15–H15H…Cl2, C1–H1…O2 and intramolecular C9–H9A…O2, C11–H11B…O2 and C14–H14B…O2 hydrogen bonds to yield a one-dimensional polymeric chain (figure 4). It is noteworthy that C1–H1…O2, C9–H9A…O2, C11–H11B…O2 and C14–H14B…O2 hydrogen bonds are rather strong with D…O distances equal to 3·175 Å, 3·328 Å, 3·262 Å and 3·180 Å, respectively, while C15–H15H…Cl2 hydrogen bond is a weak bond (C15…Cl2 distance is 3·611 Å). Moreover, in structure **5**, there are intramolecular electrostatic interaction between N(2), O(1) and O(1), Cl(2) atoms with distances of 3·012 Å and 2·980 Å, respectively.

In the structure of **8**, strong intermolecular N1–H1…O1 hydrogen bonds yield a centrosymmetric dimmer that connects to other dimers by rather strong C19–H19A…O2 and C23–H23A…Cl2 hydrogen bonds (D…O distances equal to 3·230 Å

Table 3. Selected bond lengths (Å) and angles (°) for compounds **5**, **8** and **10**.

5		**8**		**10**	
P(1)–O(2)	1·473(3)	P(1)–O(1)	1·484(1)	P(1)–O(1)	1·481(1)
P(1)–N(1)	1·708(3)	P(1)–N(1)	1·686(1)	P(1)–N(1)	1·698(1)
P(1)–N(2)	1·632(4)	P(1)–N(2)	1·6378(2)	P(1)–N(2)	1·638(2)
P(1)–N(3)	1·623(4)	P(1)–N(3)	1·630(2)	P(1)–N(3)	1·645(1)
O(1)–C(7)	1·226(4)	O(2)–C(1)	1·215(2)	O(2)–C(1)	1·221(2)
N(1)–C(7)	1·353(5)	N(1)–C(1)	1·374(2)	N(1)–C(1)	1·360(2)
C(3)–Cl(1)	1·746(4)	C(3)–Cl(1)	1·738(2)	C(3)–Cl(1)	1·738(2)
C(5)–Cl(2)	1·736(5)	C(5)–Cl(2)	1·735(2)	C(5)–Cl(2)	1·738(2)
O(2)–P(1)–N(1)	106·1(2)	O(1)–P(1)–N(1)	107·31(7)	O(1)–P(1)–N(1)	104·88(7)
O(2)–P(1)–N(2)	114·6(2)	O(1)–P(1)–N(2)	111·21(8)	O(1)–P(1)–N(2)	118·21(7)
O(2)–P(1)–N(3)	115·4(2)	O(1)–P(1)–N(3)	113·11(8)	O(1)–P(1)–N(3)	109·12(7)
N(2)–P(1)–N(1)	106·1(2)	N(2)–P(1)–N(1)	108·91(8)	N(2)–P(1)–N(1)	105·28(7)
N(1)–P(1)–N(3)	108·1(2)	N(1)–P(1)–N(3)	107·55(7)	N(1)–P(1)–N(3)	111·74(7)
N(2)–P(1)–N(3)	106·1(2)	N(2)–P(1)–N(3)	108·62(8)	N(2)–P(1)–N(3)	107·59(7)
C(7)–N(1)–P(1)	124·4(3)	C(1)–N(1)–P(1)	124·8(1)	C(1)–N(1)–P(1)	129·05(12)
C(7)–N(1)–H(1A)	117·8	C(1)–N(1)–H(1)	118·2	C(1)–N(1)–H(1N)	113·8
P(1)–N(1)–H(1A)	117·8	P(1)–N(1)–H(1)	117·0	P(1)–N(1)–H(1N)	117·0

Table 4. Hydrogen bond parameters for compounds **5**, **8** and **10** (Å, °).

Compound	(*D*–*H*…*A*)	*d* (*D*–*H*)	*d* (*H*…*A*)	*d* (*D*…*A*)	∠*DHA*
5	N(1)–H(1A)...O(2) #1	0·86	2·03	2·833	155
	N(3)–H(3)...O(1) #2	0·77	2·48	3·219	162
	C1–H(1)...O(2) #1	0·93	2·48	3·175	132
	Cl1–H(11B)...O(2)	0·96	2·58	3·262	129
	Cl5–H(15B)...Cl2(2) #2	0·96	2·83	3·611	139
8	N(1)–H(1)...O(1) #3	0·83	1·96	2·790(2)	172
10	N(1)–H(1N)...O(1) #4	0·90	1·82	2·721(2)	178

Symmetry transformations used to generate equivalent atoms: #1 1 – *x*, 2 – *y*, 1 – *z*; #2 – *x*, 2 – *y*, 1 – *z*; #3 –*x*, –*y* + 1, –*z*; #4 –*x* + 1 ,–*y* + 1, –*z*

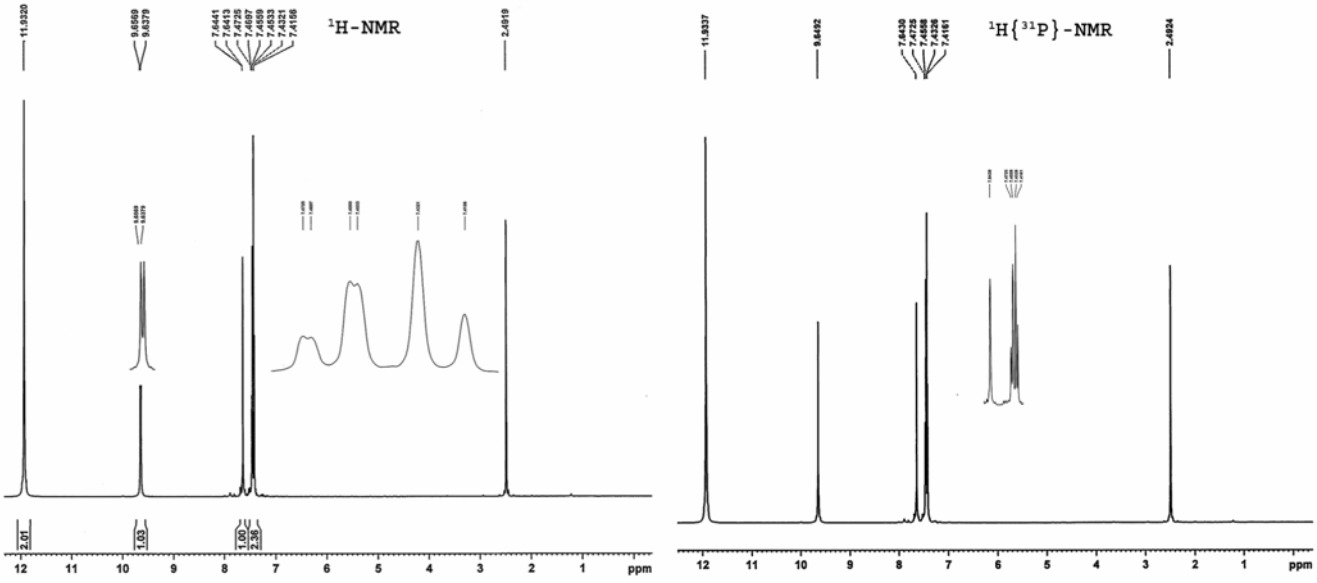


Figure 1. The ^{1}H- and ^{1}H{^{31}P} NMR spectra of compound **2**.

and 3·355 Å) plus weak intermolecular C4–H4A…O1, C16–H16B…Cl1 and C21–H21A…Cl2 hydrogen bonds (D…O distances equal to 3·463 Å, 3·639 Å and 3·734 Å) to give a three dimensional polymeric chain. There is also π–π stacking of two phenyl rings with C–C distances of 3·312 Å and an intramolecular electrostatic interaction between O(2) of C=O group and ortho Cl(1) atom with a distance equal to 2·933 Å.

Similar to **5** and **8**, in structure **10**, the strong intermolecular N1–H1N…O1 hydrogen bonds yield a centrosymmetric dimmer that attaches to other dimers through weak intermolecular C15–H15A…O2 hydrogen bonds (D…O distance is 3·424 Å) and produce a three-dimensional polymeric chain. There are also rather strong intramolecular C8–H8B…O2, C16–H16A…O2 and C18–H18B…O2 hydrogen bonds (D…O distances equal to 3·185 Å, 3·249 Å and 3·252 Å) in this network.

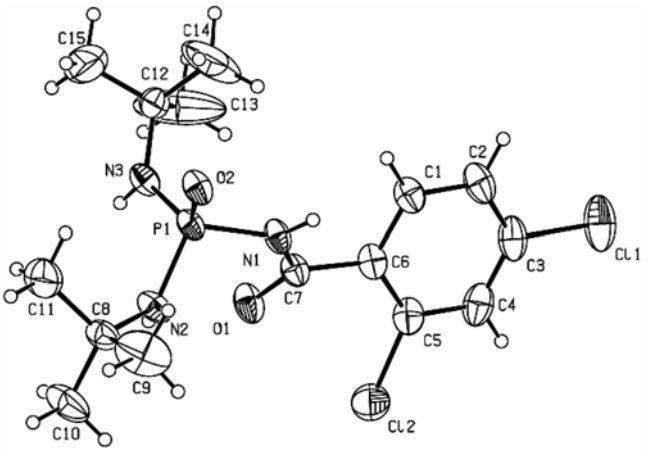


Figure 2. Molecular structure and atom labelling scheme for compound **5** (50% probability ellipsoids).

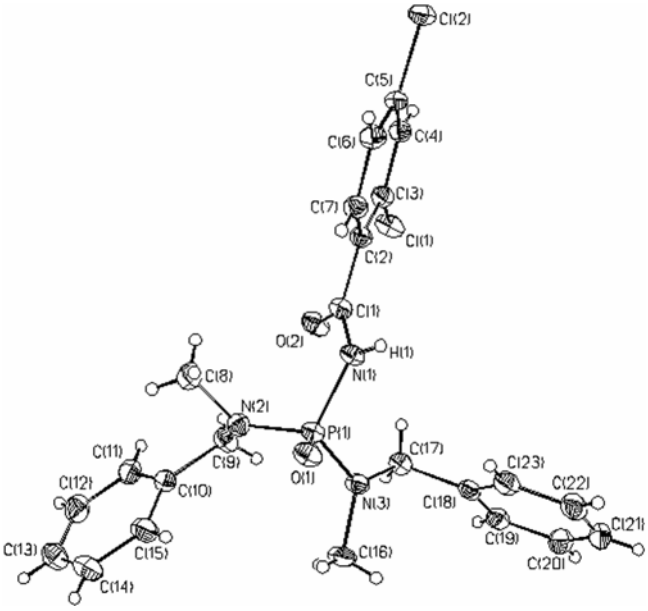


Figure 3. Molecular structure and atom labelling scheme for compound **8** (50% probability ellipsoids).

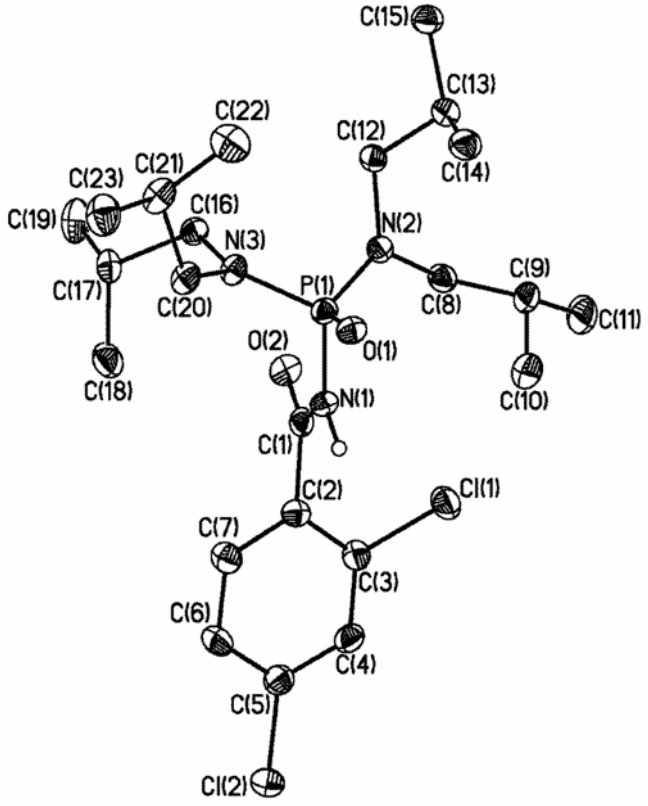


Figure 4. Molecular structure and atom labelling scheme for compound **10** (50% probability ellipsoids).

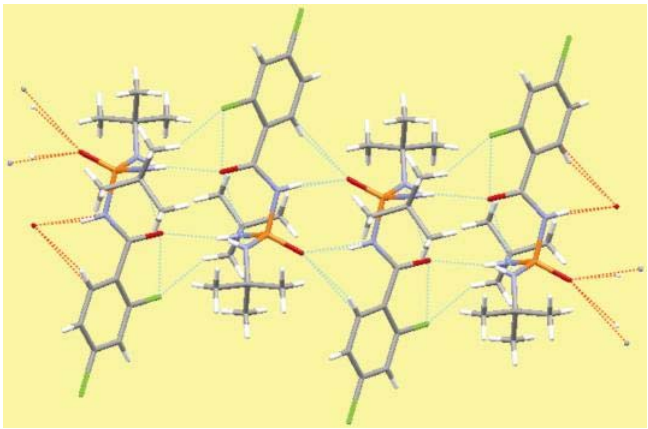


Figure 5. A one-dimensional polymeric chain produced by strong –P=O…H–N–, rather strong and weak C–H…O plus weak C–H…Cl hydrogen bonds in the crystalline lattice of compound **5**.

4. Summary

The synthesis, characterization and spectroscopic studies of some new phosphoric triamides by ^{1}H, ^{13}C, ^{31}P NMR, IR spectroscopy were performed. Long range ^{6}J (P, H) and ^{4}J (H, H) coupling constants in the range of 1·3–1·7 Hz and 1·8–1·9 Hz were observed for the coupling of aromatic protons in 2,4-dichlorophenyl rings with phosphorus atom. The spectroscopic data of newly synthesized compounds were compared with those related *N*-benzoyl derivatives. The crystal structures of three compounds were determined by X-ray crystallography that indicated intermolecular strong –P=O…H–N– as well as rather strong and weak C–H…O plus weak C–H…Cl hydrogen bonds.

Supplementary information

Supplementary data for the crystallographic data of the structures **5**, **8** and **10** have been deposited with Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 709717 ($C_{15}H_{24}Cl_2N_3O_2P$), CCDC 709122 ($C_{23}H_{24}Cl_2N_3O_2P$) and CCDC 727879 ($C_{23}H_{40}Cl_2N_3O_2P$). 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).

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