Polyhedron 29 (2010) 1612–1618

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Microwave-assisted and conventional synthesis and stereogenic properties of monospirocyclotriphosphazene derivatives

Muhammet Işıklan [a,*], Ömer Sonkaya [a], Bünyemin Çoşut [b], Serkan Yeşilot [b], Tuncer Hökelek [c]

[a] Department of Chemistry, Faculty of Science and Art, Kırıkkale University, 71450 Yahşihan-Kırıkkale, Turkey
[b] Department of Chemistry, Gebze Institute of Technology, Gebze 41400, Kocaeli, Turkey
[c] Department of Physics, Hacettepe University, 06800 Beytepe-Ankara, Turkey

ARTICLE INFO

Article history:
Received 23 December 2009
Accepted 1 February 2010
Available online 4 February 2010

Keywords:
Cyclophosphazene derivatives
Spiro-phosphazenes
Microwave-assisted synthesis
Chirality
Crystal structure

ABSTRACT

The reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with N/O donor type N-alkyl or (aryl)-o-hydroxybenzylamines $HO(C_6H_4)CH_2NHR(Ar)$, [R(Ar) = $C(CH_3)_3$ (**1**), Ph (**2**)] produce monospirocyclic tetrachlorocyclotriphosphazenes (**1a** and **2a**). The geminal substituted cyclotriphosphazenes (**1b**, **1d**, **2b** and **2d**) are obtained from the reactions of 1 equiv. of **1a** and **2a** with 2 equiv. of pyrrolidine or morpholine in THF, while the fully substituted phosphazenes (**1c**, **1e**, **2c** and **2e**) are formed from the reactions of **1a** and **2a** with the excess pyrrolidine or morpholine in toluene, between 24 and 48 h. The microwave-assisted reactions of **1a** and **2a** with excess pyrrolidine or morpholine in toluene afford the fully substituted products with higher yields than those which were obtained by conventional methods. The structural investigations of the compounds have been verified by elemental analyses, ESI-MS, FTIR, ^1H, ^{13}C, ^{31}P NMR and HETCOR techniques. The crystal structure of **2a** is determined by X-ray crystallography and the phosphazene ring is in the flattened boat form. Compounds **1b**, **1d**, **2b** and **2d** in which the spiro aryloxy moiety provides the one centre of chirality exist as racemates and the chirality has been confirmed by ^{31}P NMR spectroscopy on addition of a chiral solvating agent (CSA), (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl)ethanol.

1. Introduction

There are several studies in the literature on the reactions of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with N/O donor type difunctional reagents [1–3]. Reactions of difunctional reagents with $N_3P_3Cl_6$ may lead to a number of different types of phosphazene derivatives [4,5]. Only one of the two functional groups may react with $N_3P_3Cl_6$ to give open-chain products, and the dinucleophile may replace two chlorine atoms on two different phosphazene rings to occur bridged phosphazene architecture. In addition, spiro compounds can form if the difunctional ligand reacts with two geminal Cl atoms, and both functional groups of the ligand may replace with two Cl atoms in a cis non-geminal architecture to give trans annular substituted ansa derivatives. On the other hand, the reagents may replace with two Cl atoms on a number of different phosphazene rings to afford oligomers or polymers. Many factors, such as solvent polarities, temperature, size of the phosphazene ring and the properties of the difunctional ligands play an important role in the formation of these derivatives [6–8]. On the other hand, microwave-assisted reactions have attracted great interest in organic syntheses [9–12] as an alternative to conventional synthesis because of the advantages of direct microwave heating, repeatability and controllability [13–15]. The use of microwave irradiation for preparation of phosphazene derivatives reduces reaction time and increases yield in comparison with conventional methods.

In this study, only the spiro products (**1a** and **2a**) have been obtained. We also reported here (i) the syntheses of geminal pyrrolidino (**1b** and **2b**), and morpholino (**1d** and **2d**), and fully substituted spiro phosphazenes (**1c**, **1e**, **2c** and **2e**); (ii) the stereogenic properties of the geminal compounds (**1b**, **1c**, **2b** and **2c**) investigated by ^{31}P NMR measurements in the presence of CSA [16–18].

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Aldrich), purified by fractional crystallization from n-hexane. Morpholine (Aldrich), pyrrolidine (Fluka) and CSA (Aldrich), used without further purification. All reactions have been monitored using TLC in different solvents and chromatographed by using silica gel. ^1H, ^{13}C, and ^{31}P NMR and HETCOR spectra were recorded on Bruker DPX FT-NMR (500 MHz) spectrometer ($SiMe_4$ as internal and 85% H_3PO_4

* Corresponding author. Tel.: +90 318 3574242; fax: +90 318 3572461.
E-mail address: misiklan@gmail.com (M. Işıklan).

0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.02.002

as external standards). The spectrometer was equipped with a 5 mm PABBO BB inverse gradient probe. Standard Bruker pulse programs 1D WIN-NMR (release 6.0) and 2D WIN-NMR (release 6.1) were used in the experiment. Mass spectra were recorded on a Bruker MicrOTOF LC-MS spectrometer using the electrospray ionisation (ESI) method; ^{35}Cl values were used for calculated masses. IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr discs. Microwave-assisted experiments have been performed with a Milestone Start S system by using weflon^{TM} magnet. Numbering of atoms in phosphazene derivatives are given in Scheme 1.

2.2. Preparation of compounds

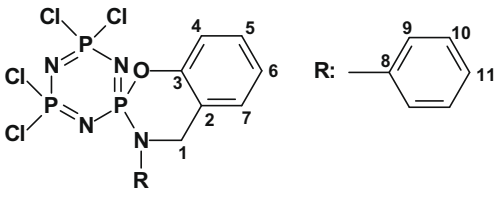
N-tert-butyl-o-hydroxybenzylamine (**1**) and N-phenyl-o-hydroxybenzylamine (**2**) have been prepared according to the methods reported in the literature [19,20].

2.2.1. 4,4,6,6-Tetrachloro-3-tert-butyl-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine][2λ^5,4λ^5,6λ^5] [1,3,5,2,4,6]triazatriphosphorine (*1a*)

A solution of **1** (1.10 g, 5.75 mmol) in THF (50 mL) and triethylamine (5.00 mL) were added to a stirred solution of $N_3P_3Cl_6$ (2.00 g, 5.75 mmol) in THF (75 mL) at room temperature. The mixture was stirred for 12 h, and the precipitated triethylamine hydrochloride was filtered off. The solvent was evaporated and the product was purified by column chromatography with toluene. White powder was crystallized from *n*-hexane. (Toluene, R_f = 0.72). Yield; 1.46 g (56%) and mp: 148 °C. *Anal.* Calc. for $C_{11}H_{15}N_4P_3OCl_4$; C, 29.10; H, 3.32; N, 12.33. Found: C, 28.59; H, 3.08; N, 12.81%., *m*/*z*: 452 (453 $[M+H]^+$). FTIR (KBr, cm^{-1}): *v* 3094; 3074 (C–H arom.), 2972; 2855 (C–H aliph.), 1245; 1176 (P═N), 579; 483 (P–Cl). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.47 (s, 9H, CH_3), 4.25 (d, 2H, $^3J_{PH}$ = 16.5 Hz, H_1), 7.12–7.19 (m, 4H, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): δ 28.84 (d, $^3J_{PC}$ = 3.8 Hz, CH_3), 45.00 (d, $^2J_{PC}$ = 2.5 Hz, C_1), 57.35 (d, $^2J_{PC}$ = 3.8 Hz, $C(CH_3)_3$), 118.38 (d, $^3J_{PC}$ = 6.3 Hz, C_4), 124.86 (C_6), 126.14 (C_7),128.15 (d, $^3J_{PC}$ = 6.3 Hz, C_2), 129.54 (C_5), 150.34 (d, $^2J_{PC}$ = 8.8 Hz, C_3).

2.2.2. 6,6-Dichloro-4,4-di(pyrrolidino)-3-tert-butyl-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine][2λ^5,4λ^5,6λ^5] [1,3,5,2,4,6]triazatriphosphorine (*1b*)

Pyrrolidine (0.36 mL, 4.40 mmol) and triethylamine (5.00 mL) were added to a stirred solution of compound **1a** (1.00 g, 2.20 mmol) in THF (100 mL) at room temperature. The mixture was refluxed for 12 h, and the precipitated triethylamine hydrochloride was filtered off. The solvent was evaporated and the product was purified by column chromatography with THF/Toluene (1:3). White powder was crystallized from n-heptane. (Toluene, R_f = 0.27). Yield; 0.75 g (65%) and mp: 159 °C. *Anal.* Calc. for $C_{19}H_{31}N_6P_3OCl_2$; C, 43.60; H, 5.97; N, 16.06. Found: C, 43.63; H, 5.93; N, 16.06%., *m*/*z*: 422 (423 $[M+H]^+$). FTIR (KBr, cm^{-1}): *v* 3094;3074 (C–H arom.), 2963;2865 (C–H aliph.), 1234;1169 (P═N), 584;480 (P–Cl). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.36 (s, 9H, $C(CH_3)_3$), 1.81 (m, 4H, NCH_2CH_2 pyrr.), 1.87 (m, 4H, NCH_2CH_2 pyrr.), 3.14 (m, 4H, NCH_2 pyrr.), 3.22 (m, 4H, NCH_2 pyrr.), 4.19 (d, 2H, $^3J_{PH}$ = 14.5 Hz, H_1), 6.96–7.13 (m, 4H, $^3J_{HH}$ = 7.8 Hz, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): δ 26.31 (d, $^3J_{PC}$ = 9.3 Hz, NCH_2CH_2 pyrr.), 26.36 (d, $^3J_{PC}$ = 9.5 Hz, NCH_2CH_2 pyrr.), 29.82 (d, $^3J_{PC}$ = 3.5 Hz, $C(CH_3)_3$). 44.75 (d, $^2J_{PC}$ = 2 6Hz, C_1), 45.95 (d, $^2J_{PC}$ = 4.3 Hz, NCH_2 pyrr.), 46.25 (d, $^2J_{PC}$ = 5.1 Hz. NCH_2 pyrr.), 56.10 (d, $^2J_{PC}$ = 3. Hz, NCH_2), 117.91 (d, $^3J_{PC}$ = 6.1 Hz, C_4), 123.54 (C_6), 125.77 (C_7), 128.65 (C_5), 128.57 (d, $^3J_{PC}$ = 7.4 Hz, C_2), δ 151.16 (d, $^2J_{PC}$ = 8.9 Hz, C_3).



Scheme 1. Numbering of atoms in phosphazene derivatives.

2.2.3. 4,4,6,6-Tetrapyrrolidino-3-tert-butyl-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ^5,4λ^5,6λ^5] [1,3,5,2,4,6]triazatriphosphorine (*1c*)

Pyrrolidine (7.00 mL, 84.6 mmol) and triethylamine (10.0 mL) were added to a stirred solution of compound **1a** (1.00 g, 2.20 mmol) in dry toluene (100 mL) at room temperature. The mixture was refluxed for 48 h, and the precipitated triethylaminehydrochloride was filtered off. The solvent was evaporated and the product was purified by column chromatography with THF/Toluene (1:3). White powder was crystallized from acetonitrile. (THF, R_f = 0.91). Yield; 0.82 g (63%) and mp: 161 °C. *Anal.* Calc. for $C_{27}H_{47}N_8P_3O$; C, 54.71; H, 7.99; N, 18.90. Found: C, 54.75; H, 7.94; N, 18.91%., *m*/*z*: 592 (593 $[M+H]^+$). FTIR (KBr, cm^{-1}): *v* 3094;3074 (C–H arom.), 2966;2851 (C–H aliph.), 1193;169 (P═N). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.66 (s, 9H, CH_3), 1.79 (m, 16H, NCH_2 pyrr.), 3.13 and 3.23 (m, 16H, NCH_2CH_2 pyrr.), 4.18 (d, 2H, $^3J_{PH}$ = 15.8 Hz, H_1), 6.90–7.21 (m, 4H, $^3J_{HH}$ = 8.7 Hz, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): δ 26.40 (d, $^3J_{PC}$ = 7.9 Hz, NCH_2CH_2 pyrr.), 29.16 (d, $^3J_{PC}$ = 3.4 Hz, CH_3), 44.86 (d, $^2J_{PC}$ = 2.0 Hz, C_1), 45.99 and 46.25 (d, $^2J_{PC}$ = 2.3 Hz, NCH_2 pyrr.), 55.23 (d, $^2J_{PC}$ = 3.4 Hz, NCH_2), 117.57 (d, $^3J_{PC}$ = 5.8 Hz, C_4), 122. 29 (C_6), 125.74 (C_7), 129.14 (C_5), 129.14 (d, $^3J_{PC}$ = 6.2 Hz, C_2), δ 152.40 (d, $^2J_{PC}$ = 9.0 Hz, C_3).

2.2.4. Microwave-assisted synthesis of *1c*

Pyrrolidine (7.00 mL, 84.6 mmol) and triethylamine (10.0 mL) were added to a stirred solution of compound **1a** (1.00 g, 2.20 mmol) in dry toluene (100 mL). The mixture was refluxed for 0.25 h, and triethylaminehydrochloride was filtered off. Toluene was evaporated and the crude product was purified by column chromatography with THF/Toluene (1:3), yield; 1.14 g (88%).

2.2.5. 6,6-Dichloro-4,4-di(morpholino)-3-tert-butyl-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ^5,4λ^5,6λ^5] [1,3,5,2,4,6]triazatriphosphorine (*1d*)

Morpholine (0.38 mL, 4.36 mmol) and triethylamine (5.00 mL) were added to a stirred solution of compound **1a** (1.00 g, 2.20 mmol) in dry toluene (100 mL) at room temperature. The mixture was refluxed for 24 h, and the precipitated triethylaminehydrochloride was filtered off. The solvent was evaporated and the product was purified by column chromatography with THF/Toluene (1:3). White powder was crystallized from *n*-hexane. (THF/Toluene (1:3), R_f = 0.40). Yield; 0.74 g (60%) and mp: 185 °C. *Anal.* Calc. for $C_{19}H_{31}N_6P_3O_3Cl_2$; C, 41.09; H, 5.63; N, 15.13. Found: C, 41.28; H, 5.39; N, 14.99%., *m*/*z*: 554 (555 $[M+H]^+$). FTIR (KBr, cm^{-1}): *v* 3094;3074 (C–H arom.), 2966;2851 (C–H aliph.), 1248;1170 (P═N), 553;489 (P–Cl). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 1.47(s, 9H, CH_3), 3.18 and 3.23 (m, 8H, NCH_2 morp.), 3.66 and 3.76 (m, 8H, NCH_2CH_2 morp.), 4.22 (d, 2H, $^3J_{PH}$ = 16.2 Hz, H_1), 6.85–7.20 (m, 4H, $^3J_{HH}$ = 8.7 Hz, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): δ 29.15 ($^3J_{PC}$ = 3.4 Hz, CH_3), 45.07 (d, $^2J_{PC}$ = 2.6 Hz, C_1), 56.68 (d, $^2J_{PC}$ = 3.6 Hz, $C(CH_3)_3$), 44.67 and 44.89 (NCH_2 morp.), 67.22 and 67.27 (d, $^2J_{PC}$ = 6.6 Hz, NCH_2CH_2 morp.), 117.94 (d, $^3J_{PC}$ = 6.2 Hz, C_4), 124.20 (C_6), 126.21 (C_7), 128.40 (d, $^3J_{PC}$ = 6.2 Hz, C_2), 129.14 (C_5), 151.02 (d, $^2J_{PC}$ = 9.0 Hz, C_3).

*2.2.6. 4,4,6,6-Tetramorpholino-3-tert-butyl-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ⁵,4λ⁵,6λ⁵] [1,3,5,2,4,6]triazatriphosphorine (**1e**)*

Morpholine (1.14 mL, 12.7 mmol) and triethylamine (10.0 mL) were added to a stirred solution of compound **1a** (1.00 g, 2.20 mmol) in dry toluene (100 mL) at room temperature. The mixture was refluxed for 48 h, and the precipitated triethylaminehydrochloride was filtered off. The solvent was evaporated and the product was purified by column chromatography with THF/Toluene (1:3). White powder was crystallized from acetonitrile. (THF, R_f = 0.91). Yield; 0.47 g (30%) and mp: 219 °C. *Anal.* Calc. for $C_{27}H_{47}N_8P_3O_5$; C, 49.38; H, 7.21; N, 17.06. Found: C, 50.00; H, 6.71; N, 16.56%., *m*/*z*: 656 (657 $[M + H]^+$). FTIR (KBr, cm^{-1}): *ν* 3094;3074 (C–H arom.), 2975;2847 (C–H aliph.), 1246;1180 (P=N). ^1H NMR: (500 MHz, $CDCl_3$, ppm): *δ* 1.49 (s, 9H, CH_3), 3.16 and 3.65 (m, 16H, NCH_2CH_2 morp.), 4.19 (d, 2H, $^3J_{PH}$ = 15.5 Hz, H_1), 6.84–7.20 (m, 4H, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): *δ* 29.46 (d, $^3J_{PC}$ = 3.3 Hz, CH_3), 44.92 and 44.86 (NCH_2 morp.), 45.03 (d, $^2J_{PC}$ = 2.4 Hz, C_1), 55.85 ($C(CH_3)_3$), 67.50 (d, $^2J_{PC}$ = 4.3 Hz, NCH_2CH_2 morp.), 117.61 (d, $^3J_{PC}$ = 5.8 Hz, C_4), 123.27 (C_6), 126.26 (C_7), 128.60 (d, $^3J_{PC}$ = 6.4 Hz, C_2), 129.26 (C_5), 151.96 (d, $^2J_{PC}$ = 9.3 Hz, C_3).

*2.2.7. Microwave-assisted synthesis of **1e***

Morpholine (1.14 mL, 12.72 mmol) and triethylamine (10.00 mL) were added to a stirred solution of compound **1a** (1.00 g, 2.20 mmol) in dry toluene (100 mL). The mixture was refluxed for 2 h., and triethylaminehydrochloride was filtered off. Toluene was evaporated and the crude product was purified by column chromatography with THF/Toluene (1:3), yield; 1.37 g (87%).

*2.2.8. 4,4,6,6-Tetrachloro-3-phenyl-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ⁵,4λ⁵,6λ⁵] [1,3,5,2,4,6]triazatriphosphorine (**2a**)*

The workup procedure was similar to that of compound **1a**, using **2** (1.15 g, 5.75 mmol) and $N_3P_3Cl_6$ (2.00 g, 5.75 mmol). (Toluene, R_f = 0.68). Yield; 0.65 g (24%) and mp: 118 °C. *Anal.* Calc. for $C_{13}H_{11}N_4P_3OCl_4$; C, 32.92; H, 2.34; N, 11.82. Found: C, 32.56; H, 2.40; N, 11.60%., *m*/*z*: 472 (473 $[M + H]^+$). FTIR (KBr, cm^{-1}): *ν* 3088;3045 (C–H arom.), 2976;2845 (C–H aliph.), 1260;1185 (P=N), 578;519 (P–Cl). ^1H NMR (500 MHz, $CDCl_3$, ppm): *δ* 4.72 (d, 2H, $^3J_{PH}$ = 15.0 Hz, H_1), 7.23–7.85 (9H, Ar–H), $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): *δ* 52.46 (d, $^2J_{PC}$ = 2.5 Hz, C_1), 119.10 (d, $^3J_{PC}$ = 8.8 Hz, C_4), 124.70 (d, $^3J_{PC}$ = 7.4 Hz, C_2), 124.80 (d, $^3J_{PC}$ = 6.30 Hz, C_9), 126.71 (C_{11}), 127.04 (C_6), 127.50 (C_7), 129.52 (C_5), 129.85 (C_{10}), 141.31 (d, $^2J_{PC}$ = 2.5 Hz, C_8), 150.25 (d, $^2J_{PC}$ = 7.5 Hz, C_3).

*2.2.9. 6,6-Dichloro-4,4-di(pyrrolidino)-3-phenyl-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ⁵,4λ⁵,6λ⁵] [1,3,5,2,4,6]triazatriphosphorine (**2b**)*

The workup procedure was similar to that of compound **1b**, using pyrrolidine (0.58 mL, 3.50 mmol) and **2a** (1.65 g, 3.50 mmol). (Toluene, R_f = 0.34). Yield; 0.38 g (20%) and mp: 158 °C. *Anal.* Calc. for $C_{21}H_{27}N_6P_3OCl_2$; C, 46.41; H, 5.01; N, 15.47. Found: C, 45.94; H, 4.76; N, 15.61%., *m*/*z*: 542 (543 $[M + H]^+$). FTIR (KBr, cm^{-1}): *ν* 3081;3019 (C–H arom.), 2974;2869 (C–H aliph.), 1243;1172 (P=N), 576;517 (P–Cl). ^1H NMR: (500 MHz, $CDCl_3$, ppm): *δ* 1.61 and 1.88 (m, 8H, NCH_2CH_2 pyrr.). 3.14 and 3.22 (m, 8H, NCH_2 pyrr.), 4.83 (d, 2H, $^3J_{PH}$ = 14.6 Hz, H_1), 7.10–7.48 (m, 9H, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): *δ* 24.19 and 24.37 (d, $^3J_{PC}$ = 9.4 Hz, NCH_2CH_2 pyrr.), 43.66 and 44.11 (d, $^2J_{PC}$ = 4.4 Hz, NCH_2 pyrr.), 50.50 (d, $^2J_{PC}$ = 2.1 Hz, C_1), 116.82 (d, $^3J_{PC}$ = 7.9 Hz, C_4), 121.66 (C_{11}), 123.12 (d, $^3J_{PC}$ = 5.7 Hz, C_2), 124.13 (d, $^3J_{PC}$ = 3.6 Hz, C_9), 124.80 (C_7), 126.79 (C_5), 127.13 (C_{10}), 141.43 (C_8), 148.98 (d, $^2J_{PC}$ = 8.5 Hz, C_3).

*2.2.10. 4,4,6,6-Tetrapyrrolidino-3-phenyl-3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ⁵,4λ⁵,6λ⁵] [1,3,5,2,4,6]triazatriphosphorine (**2c**)*

The workup procedure was similar to that of compound **1c**, using pyrrolidine (7.00 mL, 84.6 mmol) and **2a** (1.00 g, 2.11 mmol). (THF/Toluene; 1:3, R_f = 0.44). Yield; 0.45 g (31%) and mp: 210 °C. *Anal.* Calc. for $C_{29}H_{43}N_8P_3O_3$; C, 56.89; H, 7.02; N, 18.29. Found: C, 57.06; H, 6.91; N, 18.24%., *m*/*z*: 612 (613 $[M + H]^+$). FTIR (KBr, cm^{-1}): *ν* 3087;3067 (C–H arom.), 2946;2860 (C–H aliph.), 1199;1172 (P=N). ^1H NMR: (500 MHz, $CDCl_3$, ppm): *δ* 3.20 (m, 4H, NCH_2 pyrr.), 3.79 (m, 4H, $^3J_{HH}$ = 7.5 Hz, NCH_2CH_2 pyrr.), 4.74 (m, 2H, $^3J_{PH}$ = 14. Hz, $^3J_{HH}$ = 7.5 Hz, H_1), 7.15–7.44 (m, 4H, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): *δ* 44.16 (NCH_2 pyrr.), 52.39 (d, $^2J_{PC}$ = 2.5 Hz, C_1), 66.42 (d, $^3J_{PC}$ = 10.4 Hz NCH_2CH_2 pyrr.), 118.92 (d, $^3J_{PC}$ = 8.1 Hz, C_4), 124.49 (C_{11}), 125.24 (d, $^3J_{PC}$ = 5.7 Hz, C_6) 126.63 (C_5), 126.66 (d, $^3J_{PC}$ = 7.2 Hz, C_9), 126.71 (C_7), 129.28 (C_4), 129.64 (C_{10}), 142.08 (d, $^2J_{PC}$ = 2.6 Hz, C_8), 150.62 (d, $^2J_{PC}$ = 8.3 Hz, C_3).

*2.2.11. Microwave-assisted synthesis of compound **2c***

Pyrrolidine (7.00 mL, 84.6 mmol) and triethylamine (10.0 mL) were added to a stirred solution of compound **2a** (1.00 g, 2.11 mmol) in dry toluene (100 mL). The mixture was refluxed for 15 min and triethylaminehydrochloride was filtered off. Toluene was evaporated and the crude product was purified by column chromatography with THF/Toluene (1:3), yield; 1.25 g (97%).

*2.2.12. 6,6-Dichloro-4,4-di(morpholino)-3-phenyl–3,4-dihydrospiro[1,3,2-benzoxazaphosphorine][2λ⁵,4λ⁵,6λ⁵] [1,3,5,2,4,6]triazatriphosphorine (**2d**)*

The workup procedure was similar to that of compound **1d**, using morpholine (0.38 mL, 4.36 mmol) and **2a** (1.18 g, 2.50 mmol). R_f = 0.54 (THF/Toluene; 1:3). Yield; 0.25 g (19%) and mp: 178 °C. *Anal.* Calc. for $C_{21}H_{27}N_6P_3O_3Cl_2$; C, 43.83; H, 4.73; N, 14.61. Found: C, 44.02; H, 4.72; N, 15.30%., *m*/*z*: 574 (575 $[M + H]^+$). FTIR (KBr, cm^{-1}): *ν* 3090;3074 (C–H arom.), 2946;2860 (C–H aliph.), 1199;1172 (P=N), 566;485 (P–Cl). ^1H NMR: (500 MHz, $CDCl_3$, ppm): *δ* 2.60–3.19 (m, 8H, NCH_2 morp.), 3.60 and 3.74 (m, 8H, NCH_2CH_2 morp.), 4.70 (d, 2H, $^3J_{PH}$ = 14. Hz, H_1), 7.01–7.47 (m, 9H, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): *δ* 43.98 and 44.72 (NCH_2 morp.), 52.92 (C_1), 67.14 (d, $^3J_{PC}$ = 4.9 Hz, NCH_2CH_2 morp.), 118.91 (d, $^3J_{PC}$ = 7.3 Hz, C_4), 124.44 (C_9), 125.54 (C_{11}), 125.76 (d, $^3J_{PC}$ = 3.5 Hz, C_2), 126.63 (C_6), 127.14 (C_7), 128.47 (C_5) 129.28 C_{10}), 143.26 (C_8), 150.90 (d, $^2J_{PC}$ = 8.9 Hz, C_3).

*2.2.13. 4,4,6,6-Tetramorpholino-3-phenyl-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine][2λ⁵,4λ⁵,6λ⁵] [1,3,5,2,4,6]triazatriphosphorine (**2e**)*

The workup procedure was similar to that of compound **1e**, using morpholine (1.14 mL, 12.72 mmol) and **2a** (1.00 g, 2.11 mmol). R_f = 0.58 (THF/Toluene; 1:2). Yield; 1.01 g (71%) and mp: 217 °C. *Anal.* Calc. for $C_{29}H_{43}N_8P_3O_5$; C, 51.47; H, 6.40; N, 16.56. Found: C, 51.33; H, 6.34; N, 16.82%., *m*/*z*: 676 (677 $[M + H]^+$). FTIR (KBr, cm^{-1}): *ν* 3093;3070 (C–H arom.), 2958;2846 (C–H aliph.), 1204;1174 (P=N). ^1H NMR: (500 MHz, $CDCl_3$, ppm): *δ* 2.58–3.18 (m, 16H, NCH_2 morp.), 3.50 and 3.67 (m, 16H, NCH_2CH_2 morp.), 4.68 (d, 2H, $^3J_{PH}$ = 14.0 Hz, H_1), 6.96–7.48 (m, 9H, Ar–H). $^{13}C\{^1H\}$ NMR: (125 MHz, $CDCl_3$, ppm): *δ* 43.88 and 44.15 (NCH_2 morp.), 51.78 (C_1), 66.67 (d, $^3J_{PC}$ = 4.7 Hz, NCH_2CH_2 morp.), 117.82 (d, $^3J_{PC}$ = 7.1 Hz, C_4), 122.72 (C_9), 124.68 (C_{11}), 125.12 (d, $^3J_{PC}$ = 3.4 Hz, C_2), 125.37 (C_6), 125.94 (C_7), 128.10 (C_5) 128.36 (C_{10}), 143.99 (C_8), 150.78 (d, $^2J_{PC}$ = 8.7 Hz, C_3).

*2.2.14. Microwave-assisted synthesis of compound **2e***

Morpholine (1.14 mL, 12.72 mmol) and triethylamine (10.0 mL) were added to a stirred solution of compound **2a** (1.00 g,

Table 1
Crystallographic data for **2a**.

Empirical formula	$C_{13}H_{11}N_4P_3OCl_4$
Formula weight	473.97
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.868(8)
b (Å)	10.765(5)
c (Å)	11.823(6)
α (°)	68.28(4)
β (°)	69.68(5)
γ (°)	68.91(5)
V (Å^3)	948.0(11)
Z	2
μ (Mo Kα) (cm^{-1})	0.888
ρ (calcd)(g cm^{-1})	1.660
Number of reflections total	12193
Number of reflections unique	11745
R_{int}	0.0934
$2\theta_{max}$ (°)	40.00
T_{min}/T_{max}	0.806/0.878
Number of parameters	227
R [$F^2 > 2\sigma(F^2)$]	0.0781
wR	0.2835

2.11 mmol) in dry toluene (100 mL).The mixture was refluxed for 0.5 h, and triethylaminehydrochloride was filtered off. Toluene was evaporated and the crude product was purified by column chromatography with THF/Toluene (1:2), yield; 1.21 g (85%).

2.3. X-ray crystallography

Colourless crystals of **2a** were grown from n-heptane at room temperature. Crystallographic data are listed in Table 1 and selected bond lengths and angles are given in Table 3. Crystallographic data were collected on a Rigaku AFC7S diffractometer using Mo Kα radiation (λ = 0.71073 Å) at T = 294 K. Absorption correction by psi-scan [21] was applied. Structure was solved by direct methods [22] and refined by full-matrix least squares against F^2 using all data [22]. All non-H atoms were refined anisotropically. The H atom positions were calculated geometrically at distances of 0.93 (CH) and 0.97 (CH_2) Å from the parent atoms; a riding model was used during the refinement process and the U_{iso}(H) values were constrained to be 1.2 U_{eq}(carrier atom).

3. Results and discussion

3.1. Synthesis

The monospirocyclic tetrachlorocyclotriphosphazenes (**1a** and **2a**; Scheme 2) have been obtained from the reactions of N/O donor-type-N-alkyl (or aryl)-o-hydroxybenzylamines (**1** and **2**) in THF. Compounds **1a** and **2a** have four reactive chlorine atoms which can be substituted quite readily with amines. Utilising these features the geminal pyrrolidino (**1b** and **2b**) and morpholino phosphazenes (**1d** and **2d**) have been synthesized by the reactions of 1 equiv. of **1a** and **2a** with 2 equiv. of pyrrolidine and morpholine, respectively, in the presence of Et_3N in refluxing THF. In addition, the fully substituted phosphazenes (**1c** and **2c**) and (**1e** and **2e**) have been obtained from the reactions of **1a** and **2a** with the excess pyrrolidine and morpholine in toluene, respectively (Scheme 2). According to the conventional method monospirocyclic derivatives (**1a** and **2a**) and geminal alkylamino spirocyclotriphosphazenes (**1b**, **1d**, **2b** and **2d**) have been synthesized with the yields in a range of 45–65%. The fully substituted (**1c**, **1e**, **2c** and **2e)** derivatives have been obtained with the yields in a range of 30–71%, whilst the yields of microwave assisted reactions are very high (85–97%). The use of microwave is very helpful to improve the yields and to decrease the reaction time. As expected, in the microwave assisted synthesis of **1c** and **1e** which contain bulky substituents bonded to nitrogen atom of *spiro*-ring, the reaction time is longer than that of **2c** and **2e**.

The microanalyses, FTIR, MS and NMR data are consistent with the proposed structures of the compounds. All of the new phosphazene derivatives show the protonated molecular ion ($M + H^+$) peaks.

3.2. FTIR and NMR spectroscopy

The asymmetric and symmetric stretching absorptions of the Ar–H protons are observed at the ranges of 3075–3052 cm^{-1} and 3040–3024 cm^{-1}, respectively. The FTIR spectra of all the phosphazenes exhibit strong stretching bands between 1240 and 1170 cm^{-1} attributed to $\nu_{P=N}$ bonds of the phosphazene ring [23,24]. In addition, the asymmetric and symmetric absorption

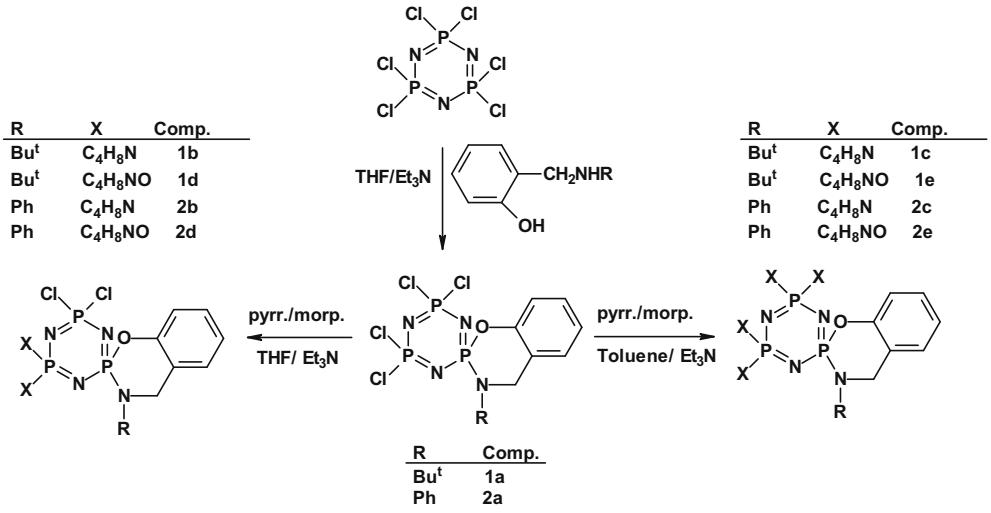
Table 2
^{31}P NMR parameters of compounds and the effect of CSA on ^{31}P NMR chemical shifts.[a]

Compound	Spin system	>PX_2	>PCl_2	>P(ORN)	X or X_2	^2J(PP)/Hz		
		1	2	3		1,2	1,3	2,3
(i) ^{31}P NMR chemical shifts (ppm) and geminal PNP coupling constants (Hz)								
1a	AX_2		23.39	5.59	Cl			54.6
2a	AX_2		24.73	3.80	Cl			56.6
1b	AMX	14.86	25.49	10.07	C_4H_8N	48.5	49.6	57.8
2b	AMX	17.16	25.71	8.19	C_4H_8N	45.0	51.1	58.9
1c	AX_2	18.13		16.66	C_4H_8N		47.2	-
2c	AX_2	19.61		14.95	C_4H_8N		48.9	-
1d	AMX	17.83	25.30	10.67	C_4H_8NO	55.2	48.5	55.9
2d	AMX	19.33	25.72	8.02	C_4H_8NO	49.3	52.3	57.2
1e	AX_2	23.04		16.44	C_4H_8NO		47.5	
2e	AX_2	22.13		13.60	C_4H_8NO		50.5	
(ii) Change in chemical shifts (ppb) at CSA:compound mole ratio of 30:1								
1b		−4.0	291.7	151.5	C_4H_8N	46.9	47.6	56.8
2b		45	144.5	73	C_4H_8N	43.7	51.9	57.5
1d		−108	116.5	−4.5	C_4H_8NO	58.3	58.5	55.0
2d		−190	150	−4.2	C_4H_8NO	48.7	50.8	56.5
(iii) Separation of signals of enantiomers (ppb) at CSA:compound mole ratio of 30:1								
1b		212	141	95	C_4H_8N			
2b		38	149	28	C_4H_8N			
1d		70	55	25	C_4H_8NO			
2d		80	200		C_4H_8NO			

[a] 202.38 MHz ^{31}P NMR measurements in $CDCl_3$ solutions at 298 K.

Table 3
The selected bond lengths (Å) and angles with the selected torsion angles (°) for **2a**.

P1–N1	1.600(3)	P1–N3	1.583(3)	P2–N1	1.563(3)
P2–N2	1.585(3)	P3–N2	1.576(3)	P3–N3	1.569(3)
P1–N4	1.637(3)	P1–O1	1.581(2)		
N1–P1–N3	115.28(15)	N1–P2–N2	119.23(16)	N2–P3–N3	119.73(15)
P1–N1–P2	122.90(17)	P2–N2–P3	119.34(18)	P1–N3–P3	122.57(18)
N3–P1–N4	110.81(16)	N3–P1–O1	107.01(15)	N1–P1–N4	112.30(15)
N1–P1–O1	107.51(17)	O1–P1–N4	102.97(13)	P1–N4–C7	118.5(3)
P1–N4–C8	117.10(19)	C7–N4–C8	115.5(2)		
N3–P1–N1–P2	6.6(3)	O1–P1–N3–P3	−130.3(2)	N2–P2–N1–P1	1.7(3)
N4–P1–N1–P2	−121.6(2)	N1–P1–N3–P3	−10.8(3)	N2–P3–N3–P1	6.6(3)



Scheme 2. The chloride replacement reaction pathway of $N_3P_3Cl_6$ with the nucleophiles.

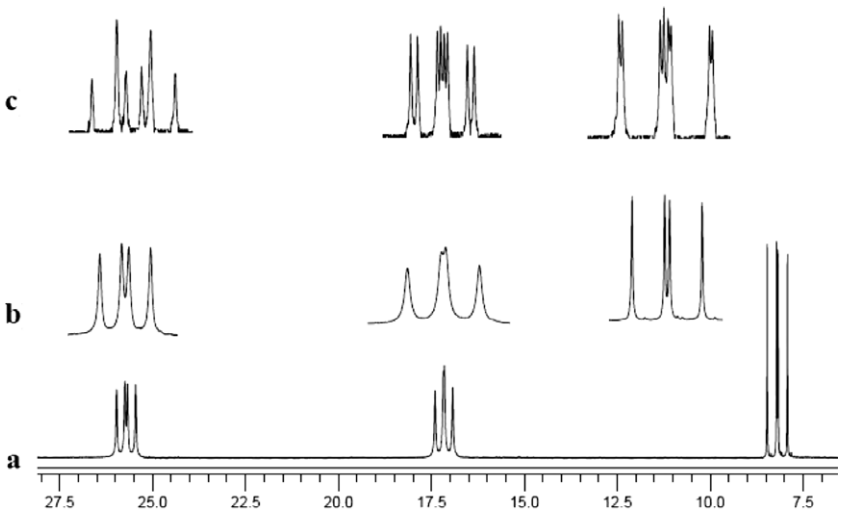


Fig. 1. ^{31}P NMR spectra of **2b** (a) in $CDCl_3$, (b) expansion of signals showing AMX spin system, (c) addition of CSA at *ca.* 30:1 mol ratio shows the doubling of signals which is characteristic for a racemate.

bands of ν_{PCl2} have arisen for the tetrachloro (**1a** and **2a**) and dichloro (**1b**, **1d**, **2b** and **2d)** phosphazenes in the ranges of 584–553 cm^{-1} and 519–480 cm^{-1}, respectively.

The ^1H-decoupled ^{31}P NMR data of the phosphazenes are given in Table 2. The data indicated that all of the phosphazenes have spiro structures. The spin systems are interpreted as AX_2 for **1a**, **1c**, **1e**, **2a**, **2c** and **2e** and AMX for **1b**, **1d, 2b**, and **2d** (Table 2). As an example, the proton-decoupled ^{31}P NMR spectrum of compound **2b** is shown as the expected AMX spin system in Fig. 1a. Signal assignment of the representative compound **2b** is straightforward with the quartet at ca 25.71 ppm belonging to $>PCl_2$, the quartet at ca. 17.16 ppm to $>P(Pyrr)_2$ and the quartet at ca. 8.19 ppm to >P(ORN) (Table 2). Fig. 2 illustrates the spatial view of the architectures for better understanding. Compounds

1a, **1c**, **1e**, **2a**, **2c** and **2e** show a typical five lines resonance pattern consisting of a triplet for one P (spiro) atom and a doublet for two other P atoms. The geminal phosphazenes, **1b**, **1d**, **2b** and **2d** show a 12-lines resonance pattern consisting of a doublet of doublets for all of the P atoms. The coupling constants of all the compounds are between 45.0 and 58.9 Hz. Compounds **1a**, **1c**, **1e**, **2a**, **2c** and **2e** have the planes of symmetry, whereas compounds **1b**, **1d**, **2b** and **2d** in which the spiro aryloxy moiety provides the one centre of chirality are asymmetrical. As expected, these compounds containing one stereogenic centre exist as racemates and their enantiomers have been analysed by changes in the ^{31}P NMR spectra on addition of a chiral solvating agent, (S)-(+)-2,2,2-trifluoro-1-(9′-anthryl)ethanol, (CSA) [6,25–27]. On titration with CSA, the chemical shifts change as a result of the equilibrium between the compound and its ligand-complexed form and the changes (in ppb) at a mole ratio of CSA:compound of 30:1 are summarised in Table 2. In general, there are changes in both ^{31}P NMR chemical shifts (expressed in ppb) and magnitudes of geminal ^{2}J(PP) coupling constants. On titration with CSA, some of the signals in each of the compounds **1b**, **1d**, **2b** and **2d** separate into two signals of equal intensity corresponding to the different effects on the two enantiomers. These results confirmed that cyclotriphosphazene derivatives containing one stereogenic centre exist as racemates. The spectra of **2b** are depicted in Fig. 1 for comparison. Addition of CSA at a 30:1 molar ratio causes the separations of all signals into two lines of equal intensity indicating that **2b** exists as a racemate. The separations in chemical shifts (in ppb) of enantiomers are given separately in Table 2 for compounds **1b**, **1d**, **2b** and **2d**.

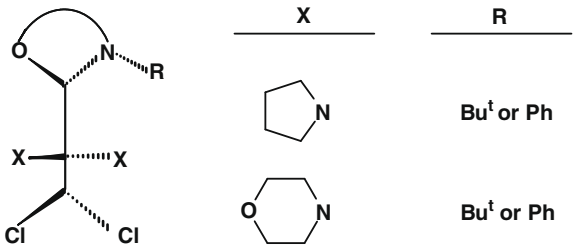


Fig. 2. Spatial view of **1b, 1d, 2b** and **2d**.

The ^{1}H and ^{13}C{^{1}H} NMR signals have been assigned on the basis of chemical shifts, multiplicities and coupling constants using the data of ^{1}H, ^{13}C{^{1}H} NMR and HETCOR spectra for the phosphazene derivatives. The protons of the benzylic moieties, Ar–CH_2N give rise to doublets and the multiplets for **1a**, **1c**, **1d**, **1e**, **2a**, **2c**, **2e** and **1b**, **2b**, **2d**, respectively. The geminal Ar–CH_2N protons of **1b**, **2b** and **2d** are not equivalent to each other; therefore, they give two groups of multiplets with small separations. The $^{3}J_{PH}$ values of Ar–CH_2N protons are between 14.0 and 16.2 Hz. The signals of methyl protons of **1a**, **1b**, **1c**, **1d** and **1e** are observed as singlets in the range of 1.36–1.66 ppm. In the ^{1}H NMR spectra of geminal

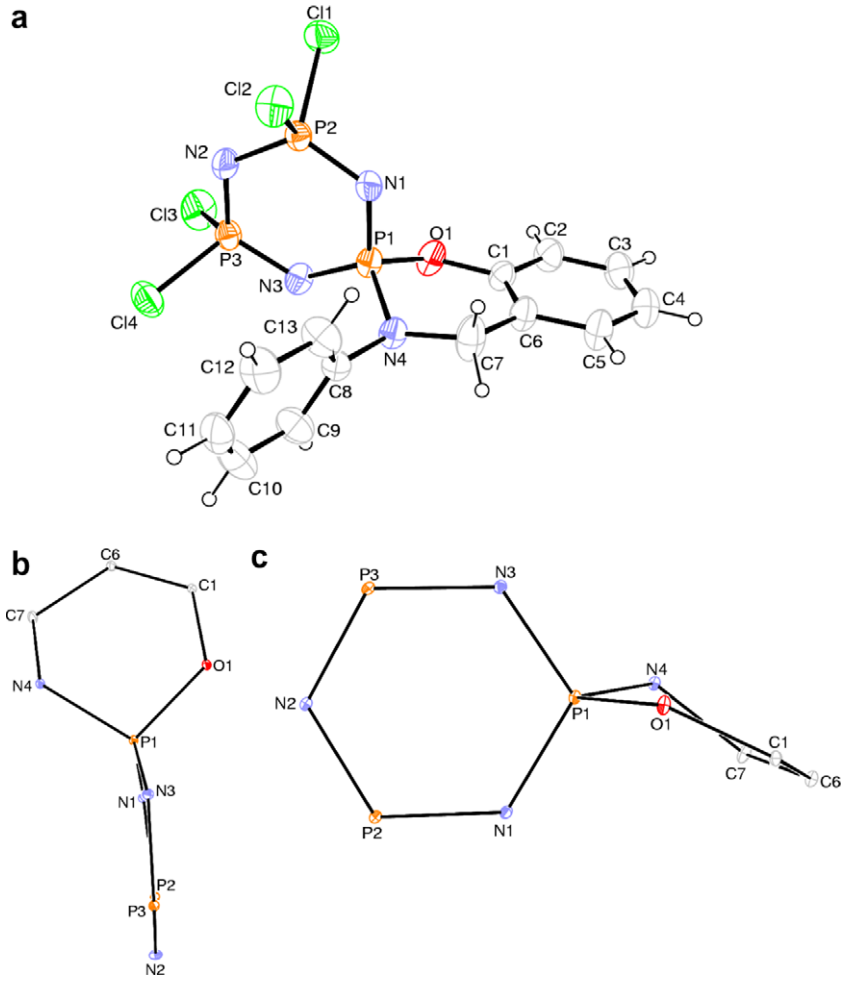


Fig. 3. (a) An ORTEP-3 [33] drawing of **2a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, (b) the conformation of the phosphazene ring, and (**c**) the conformation of the six-membered *spiro*-ring.

phosphazenes **1b**, **1d**, **2b** and **2d**; the two pyrrolidino or morpholino substituents bonded to the same P atom show two groups of NCH_2 signals with small separations. As expected, the same situation is observed for NCH_2CH_2 protons. All of the expected carbon signals are interpreted from the $^{13}C\{^1H\}$ NMR spectra of the phosphazenes. The NCH_2 signals of **1b**, **1c**, **1d**, **1e**, **2b**, **2c**, **2d** and **2e** are confirmed by HETCOR experiments; for NCH_2 (pyrr.) and Ar–CH_2. The expected coupling constants between aromatic C atoms and P atoms are observed for C_1, C_2, C_3 and C_4 as doublets (see experimental part). In the $^{13}C\{^1H\}$ NMR spectra of geminal phosphazenes **1b**, **1d**, **2b** and **2d,** the two pyrrolidino or morpholino substituents bonded to the same P atom show two groups of NCH_2CH_2 carbons indicating different environments (Fig. 2).

3.3. X-ray structure of *2a*

The solid state structure of compound 2a confirms the assignments of its structure from spectroscopic data. The molecular structure of 2a along with the atom-numbering scheme is depicted in Fig. 3a. The phosphazene ring of 2a is not planar and is in flattened boat form [Fig. 3b; φ_2 = 152.5(1.3)° and θ_2 = 102.1(1.3)°] having total puckering amplitude [28] Q_T of 0.107(3) Å. The N atoms are displaced above (+) and below (−) the least squares plane through the P atoms by the following distances: N1 − 0.022(3), N2 0.088(4) and N3 − 0.118(3) Å. As expected in 2a, six-membered *spiro*-ring is in nearly twisted form [Fig. 3c; φ_2 = 55.8(2)° and θ_2 = 111.8(2)°] having total puckering amplitude [28] Q_T of 0.193(11) Å. The sum of the bond angles around the atom N4 [351.1(2)°] shows the change in hybridization of the atom slightly from trigonal planar towards pyramidal. The pyramidality of N4 atom especially may depend on the conformations of phosphazene and *spiro*-rings (Fig. 3b and c).

In the phosphazene ring, the endocyclic P–N bonds are in the range of 1.563(3)–1.600(3) Å and has an average value of 1.579(3) Å, which is shorter than the exocyclic P–N bond of 1.637(3) Å (Table 3). The phosphazene ring P–N bonds show double-bond character. In addition, exocyclic P–N bond is at the lower limit of the single-bond length. In phosphazenes, the PN single and double-bonds are estimated to be in the ranges of 1.628–1.691 and 1.571–1.604 Å, respectively [29]. Recently, multiple-bond character of the PN bonds in the phosphazene ring are attributed to the presence of negative hyperconjugation [30,31]. As can be seen from Table 2; endocylic N1–P1–N3 (α) angle is narrowed, and P1–N1–P2 (β) and N1–P2–N2 (γ) angles are expanded slightly with respect to the corresponding values in the "standard" compound, $N_3P_3Cl_6$. In $N_3P_3Cl_6$, the α, β, γ and δ angles are 118.3(2)°, 121.4(3)°, 118.3(2)° and 121.4(3)°, respectively [32]. The changes in the angles of phosphazene derivatives could be attributed to the substituent dependent charges at the *P* centres and negative hyperconjugation [30]. The planar rings (C1–C6) and (C8–C13) are oriented at a dihedral angle of 76.6(1)°.

4. Conclusions

N/O donor type ligands which are N-tert-butyl-o-hydroxybenzylamine (**1**) and N-phenyl-o-hydroxybenzylamine (**2**) have led to the formation of monospirocyclotriphosphazene (**1a** and **2a**) architectures via the condensation reactions of $N_3P_3Cl_6$. The substitution reactions of monospirocyclotriphosphazene derivatives with the pyrrolidine or morpholine produce the geminal (**1b**, **1d**, **2b** and **2d**) and fully substituted (**1c**, **1e**, **2c** and **2e**) derivatives. The fully substituted cyclotriphosphazenes are also obtained using microwave, compared with those from the conventional methods. The use of microwave is really helpful to improve the yields and reduce the reaction times. The enantiomers of geminal monospirocyclotriphosphazenes have been determined by the changes in the ^{31}P NMR spectra on addition of a Chiral Solvating Agent (CSA), (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl)ethanol. These results confirmed that geminal monospirocyclotriphosphazenes containing one centre of chirality exist as racemates. The fully substituted cyclotriphosphazene derivatives may also be ligating agents for some transition metal cations.

5. Supplementary data

CCDC 758922 contains the supplementary crystallographic data for **2a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Acknowledgements

The authors acknowledge the "Scientific and Technical Research Council of Turkey; TÜBİTAK" (Grant No. 106T503). T.H. is indebted to "Hacettepe University, Scientific Researchs Unit" Grant No. 02 02 602 002 for financial support.

References

[1] E.E. İlter, N. Asmafiliz, Z. Kılıç, M. Işıklan, T. Hökelek, N. Çaylak, E. Şahin, Inorg. Chem. 46 (2007) 9931.
[2] H. Dal, Y. Süzen, Spectrochim. Acta, Part A 67 (2007) 1392.
[3] S. Bilge, Ş. Demiriz, A. Okumuş, Z. Kılıç, B. Tercan, T. Hökelek, O. Büyükgüngör, Inorg. Chem. 45 (2006) 8755.
[4] H.R. Allcock, M.L. Turner, K.B. Visscher, Inorg. Chem. 31 (1992) 4354.
[5] C.W. Allen, Coord. Chem. Rev. 130 (1994) 137.
[6] V. Chandrasekhar, S. Karthikeyan, S.S. Krishnamurthy, M. Woods, Indian J. Chem. 24A (1985) 379.
[7] H.R. Allcock, U. Diefenbach, S.R. Pucher, Inorg. Chem. 33 (1994) 3091.
[8] V. Chandrasekhar, V. Krishnan, Adv. Inorg. Chem. 53 (2002) 159.
[9] C. Kantar, E. Ağar, S. Şaşmaz, Polyhedron 28 (2009) 3485.
[10] R. Sharma, S.K. Vadivel, R.I. Duclos Jr, A. Makriyannis, Tetrahedron Lett. 50 (2009) 5780.
[11] M. Pinerio, T.M.V.D. Pinho e Melo, Eur. J. Org. Chem. (2009) 5287.
[12] S. Caddick, R. Fitzmaurice, Tetrahedron 65 (2009) 3325.
[13] C.O. Kappe, D. Dallinger, Mol. Diversity 13 (2009) 71.
[14] J.P. Tierney, P. Lidström (Eds.), Microwave Assisted Organic Synthesis, Blackwell, Victoria, 2005.
[15] V. Polshhettiwar, R.S. Varma, Chem. Soc. Rev. 37 (2008) 1546.
[16] N. Asmafiliz, Z. Kılıç, A. Öztürk, T. Hökelek, L.Y. Koç, L. Açık, Ö. Kısa, A. Albay, Z. Üstündağ, A.O. Solak, Inorg. Chem. 48 (2009) 10102.
[17] B. Çoşut, H. İbişoğlu, A. Kılıç, S. Yeşilot, Inorg. Chim. Acta 362 (2009) 4931.
[18] S. Yeşilot, B. Çoşut, Inorg. Chem. Commun. 10 (2007) 88.
[19] E. Modica, R. Zanaletti, M. Freccero, M. Mella, J. Org. Chem. 66 (2001) 41.
[20] R. Andreu, J.C. Ronda, Synth. Commun. 38 (2008) 2316.
[21] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., Sect. A 24 (1968) 351.
[22] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[23] G.A. Carriedo, F.G. Alonso, P.A. Gonzalez, J.R. Menendez, J. Raman Spectrosc. 29 (1998) 327.
[24] E.E. İlter, N. Çaylak, M. Işıklan, N. Asmafiliz, Z. Kılıç, T. Hökelek, J. Mol. Struct. 697 (2004) 119.
[25] S.J. Coles, D.B. Davies, R.J. Eaton, M.B. Hursthouse, A. Kılıç, R.A. Shaw, Ş. Şahin, A. Uslu, S. Yeşilot, Inorg. Chem. Commun. 7 (2004) 657.
[26] S. Beşli, S.J. Coles, D.B. Davies, R.J. Eaton, M.B. Hursthouse, A. Kılıç, R.A. Shaw, A. Uslu, S. Yeşilot, Inorg. Chem. Commun. 7 (2004) 842.
[27] S.J. Coles, B. Davies, R.J. Eaton, A. Kılıç, R.A. Shaw, G. Yenilmez Çiftçi, Polyhedron 25 (2006) 953.
[28] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
[29] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 1 2 (1987) 1.
[30] A.B. Chaplin, J.A. Harrison, P.J. Dayson, Inorg. Chem. 44 (2005) 8407.
[31] S.S. Krishnamurthy, Phosphorus, Sulfur Silicon Relat. Elem. 87 (1994) 101.
[32] G.J. Bullen, J. Chem. Soc. A (1971) 1450.
[33] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.