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Synthesis of a New Class of Fused Cyclotetraphosphazene Ring Systems

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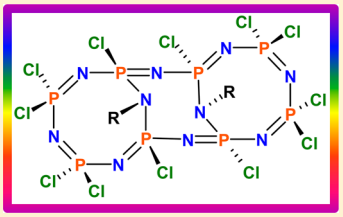
Supporting Information

ABSTRACT: Octachlorocyclotetraphosphazene (**1**) was reacted with butylamines [*n*-butyl, *i*-butyl, *sec*-butyl, and *t*-butyl] in a 1:0.8 mol ratio in THF to obtain cyclotetraphosphazenes bearing a P-NH group, $N_4P_4Cl_7(NHR)$ [R = *n*-butyl (**2a**), *i*-butyl (**2b**), *sec*-butyl (**2c**), *t*-butyl (**2d**)](**2a**–**d**). The cyclotetraphosphazene derivatives **2a**, **2b**, and **2c** were treated with sodium hydride giving rise to a new type of cyclophosphazene compounds (P_8N_8 ring) consisting of three fused tetramer rings (**3a**–**c**). Whereas reaction of sodium hydride with the *t*-butylaminocyclophosphazene derivative (**2d**) gave a P–O–P bridged compound (**4**) presumably as a result of hydrolysis reaction associated with moisture in the solvent. It is likely that the 16-membered cyclooctaphosphazene derivatives (**3a**–**c**) are formed by a proton abstraction/chloride ion elimination, intramolecular nucleophilic attack, ring opening and intermolecular condensation processes, respectively.



INTRODUCTION

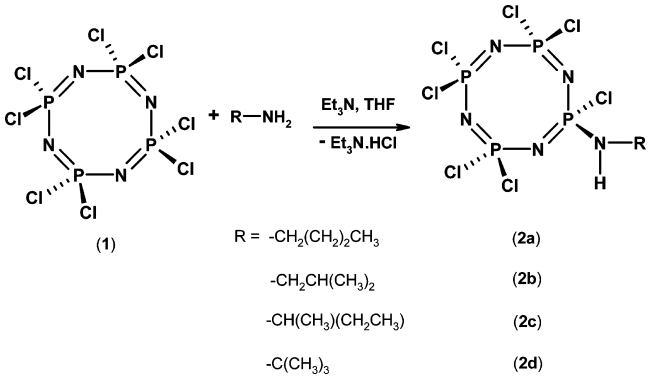
Heterocyclic cyclophosphazenes have numerous applications,[1−11] such as biomedical materials,[1] flame retardants,[2] liquid crystals,[3,4] lubricants,[5] electrical conductors,[6] rechargeable batteries,[7] and coordination chemistry.[8,9] This in turn has stimulated the development of, and interest in, new heterocyclic cyclophosphazene structural types by both the academic and industrial communities.[12−18] The rigid stereochemistry at the phosphorus centers is one of the most important features of these compounds. Also, the different functionalities at the phosphorus centers make these heterocyclic compounds fascinating with respect to both structural and electronic properties.

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) is the most popular compound in the cyclophosphazene series, and its reactions have been studied in great detail.[1−8,10−18] There are far fewer studies of the reactions of the corresponding octachlorocyclotetraphosphazene ($N_4P_4Cl_8$).[9,19−23] The reactions of $N_4P_4C1_8$ are more complex due to the greater number of possible products, and the resulting products have a wider range of structural possibilities due to skeletal flexibility of the eight-membered ring.[21−23]

Recently, we have developed a new synthetic route for the preparation of heterocyclic structures having a P–N backbone including bis-cyclophosphazenes bridged with a four-membered cyclophosphazane ring in a spiro arrangement and an eight-membered cyclophosphazene ring in an ansa arrangement as well as asymmetrically bridged cyclophosphazenes by deprotonation reactions of amino cyclotriphosphazene derivatives.[24−26] Furthermore, deprotonation of a cyclotriphosphazene with a bulky group such as *t*-butylamino in the side chain results in the formation of a nearly planar cyclohexaphosphazene derivative by a ring expansion during the reaction.[26]

The interesting structures obtained by deprotonation reactions of cyclotriphosphazene derivatives containing a P–NH group in the side chain prompted us to investigate this reaction with analogous cyclotetraphosphazene derivatives. Therefore, we studied the deprotonation reactions of mono amino cyclotetraphosphazene derivatives (**2a**–**d**) (Scheme 1)

Scheme 1. Synthesis of Compounds 2a–d



and compared the results to previous work.[26] Deprotonation reactions of *n*-butyl–, *i*-butyl– and *sec*-butylaminocyclotetraphosphazenes (**2a**–**c**) lead to the first formation of the new fused ring cyclooctaphosphazene (**3a**–**c**) as shown in Scheme 2. However, the *t*-butylaminocyclotetraphosphazene derivative (**2d**) hydrolyzed during the deprotonation reaction leads to an oxo bridged dimer (Scheme 3).

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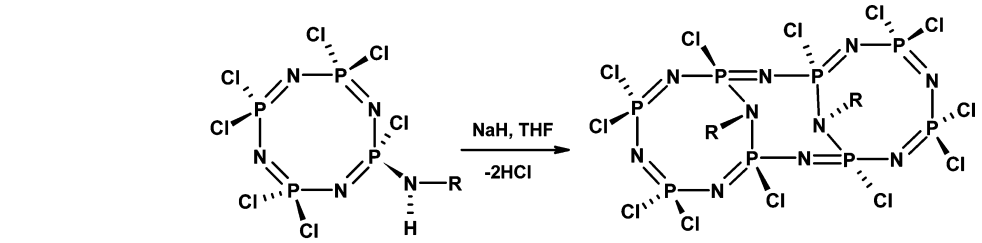
Scheme 2. Synthesis of Compounds 3a−c

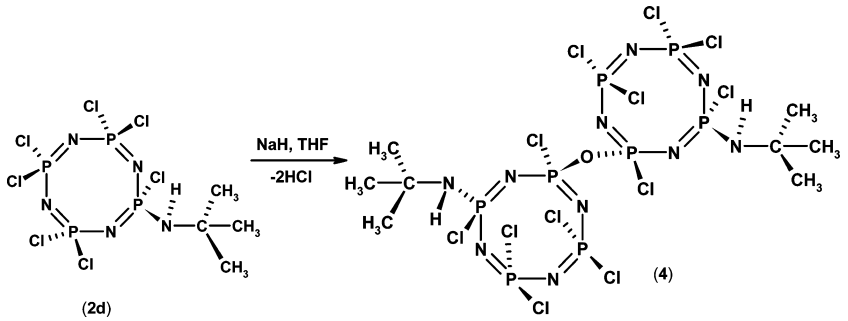


R = $-CH_2(CH_2)_2CH_3$ (2a) (3a)

$-CH_2CH(CH_3)_2$ (2b) (3b)

$-CH(CH_3)(CH_2CH_3)$ (2c) (3c)

Scheme 3. Synthesis of Compound 4



(2d) (4)

EXPERIMENTAL SECTION

Materials. Octachlorocyclotetraphosphazene (Otsuka Chemical Co., Ltd.) was purified by fractional crystallization from *n*-hexane. Dichloromethane (Merck), triethylamine (Merck), *n*-hexane (Merck), *n*-butylamine (Merck), *i*-butylamine (Merck), *sec*-butylamine (Aldrich), *t*-butylamine (Merck), 1,8,9-antracenetriol (A. Aesar), and 2,5-dihydroxybenzoic acid (Merck) were used as received. THF (Merck) was distilled over Na−K alloy in an argon atmosphere. Sodium hydride was dispersed 60% in mineral oil (Merck), and prior to use, the oil was removed by washing with dry *n*-hexane followed by decantation. $CDCl_3$ for NMR spectroscopy was also obtained from Merck. Analytical Thin Layer Chromatography (TLC) was performed on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230−400 mesh; for 3 g of crude mixture, 100 g of silica gel was used).

Methods. Elemental analyses were obtained using ElementarVario MICRO Cube. Mass spectra were recorded on a Bruker MicrOTOF LC/MS spectrometer using electro spray ionization (ESI) method for compounds **2c**, **2d**, and **4**; ^{35}Cl values were used for calculated masses. It was observed that these molecules had seven chlorine atoms. Mass analyses were recorded on a Bruker MALDI−TOF (Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight) spectrometer using 2,5-dihydroxybenzoic acid as a matrix for compounds **2a**, **2b**, **3a**, **3b** and 1,8,9-antracenetriol as the matrix for compound **3c**. ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ^1H and 85% H_3PO_4 as an external reference for ^{31}P. The free trial version of the gNMR 4.1 spectral simulation program (from Adept Scientific) was used for calculation of all coupling constants.

X-ray Crystallography. Intensity data were recorded on a Bruker APEX II QUAZAR diffractometer. Absorption correction by multiscan was been applied,[27] and space groups were determined using XPREP implemented in APEX2.[28] Structures were determined using the direct methods procedure in SHELXS-97 and refined by full-matrix least-squares on F2 using SHELXL-97.[29] All non-hydrogen atoms were refined with anisotropic displacement factors, and C−H hydrogen atoms were placed in calculated positions and allowed to ride on the parent atom. The final geometrical calculations and the molecular drawings were carried out with PLATON,[30] MERCURY,[31] and DIAMOND (Version 3.1)[32] programs. Structure determinations have been deposited with the Cambridge Crystallographic Data Centre with references CCDC 973128, 973129, and 1025485 for structures **3b**, **3c**, and **4** respectively.

Syntheses of 2-Amino-2,4,4,6,6,8,8-heptachlorocyclotetraphosphazenes (2a−d). Octachlorocyclotetraphosphazene, (**1**) (2.000 g, 4.31 mmol) and triethylamine (0.349 g, 3.45 mmol) were dissolved in 300 mL of dry THF in a 500 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and the appropriate amine (*n*-butylamine/*i*-butylamine/*sec*-butylamine/*t*-butylamine) (0.252 g, 3.45 mmol) in 10 mL of dry THF was dropped into a stirred solution under an argon atmosphere. The reaction was stirred for an additional 4 h at room temperature and followed by TLC on silica gel plates using *n*-hexane−dichloromethane (5:1) which showed one new product. The reaction mixture was filtered; the solvent was removed under reduced pressure, and the crude product was subjected to column chromatography using *n*-hexane−dichloromethane as the eluent. The first compound of the column was unreacted compound **1** and the second was the 2-amino-2,4,4,6,6,8,8-heptachlorocyclotetraphosphazenes (**2a−d**) was isolated as an oil.

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2a: Yield: 1.29 g, 75%. Anal. Calcd for $C_4H_{10}Cl_7N_5P_4$: C, 9.60; H, 2.02; N, 14.0%, M, 500.2. Found: C, 12.52; H, 2.15; N, 12.79%. MALDI-TOF-MS (m/z): $[M + H]^+$, 501.7. ^{1}H NMR ($CDCl_3$, 298 K); δ (ppm) 0.88 (t, 3H, $-CH_3$, $^3J_{H-H}$ = 7.4 Hz), 1.33 (m, 2H, -CH_2-CH_3, $^3J_{H-H}$ = 7.5 Hz), 1.49 (q, 2H, $-CH_2-$,$^3J_{H-H}$ = 7.2 Hz), 2.99 (m, 2H, $-CH_2$-NH, $^3J_{H-H}$ = 6.7 Hz, $^2J_{P-H}$ = 13.3 Hz), 3.12 (br, 1H, NH). ^{31}P NMR ($CDCl_3$, 298 K) ; AM_2X spin system, δ (ppm) −3.54 [PCl(NHR)], −5.37 [$2PCl_2$], −8.00 [PCl_2], $^2J_{PCl(NHR)PCl2}$ = 36.8 Hz, $^2J_{PCl2PCl2}$ = 32.0 Hz.

2b: Yield: 1.21 g, 70%. Anal. Calcd for $C_4H_{10}Cl_7N_5P_4$: C, 9.60; H, 2.02; N, 14.0%, M, 500.2. Found: C, 12.53; H, 2.54; N, 13.54%. MALDI-TOF-MS (m/z): $[M + H]^+$, 501.0. ^{1}H NMR ($CDCl_3$, 298 K); δ (ppm) 0.97 (d, 6H, $-CH_3$,$^3J_{H-H}$ = 6.7 Hz), 1.82 (m, 1H, $-CH-$, $^3J_{H-H}$ = 6.7 Hz), 2.87 (q, 2H, $-CH_2-$, $^3J_{H-H}$ = 6.8 Hz, $^2J_{P-H}$ = 12.6 Hz), 3.22 (br, 1H, NH).^{31}P NMR ($CDCl_3$, 298 K); AM_2X spin system, δ (ppm) −3.18 [PCl(NHR)], −5.45 [$2PCl_2$], −7.97 [PCl_2], $^2J_{PCl(NHR)PCl2}$ = 37.2 Hz, $^2J_{PCl2PCl2}$ = 31.9 Hz.

2c: Yield: 1.09 g, 63%. Anal. Calcd for $C_4H_{10}Cl_7N_5P_4$: C, 9.60; H, 2.02; N, 14.0%, M, 500.2. Found: C, 11.90; H, 2.35; N 12.99%. ESI-MS (m/z): $[M-2H]^+$, 497.9. ^{1} H NMR ($CDCl_3$, 298 K); δ (ppm) 0.89 (t, 3H, $-CH_2-CH_3$, $^3J_{H-H}$ = 7.4 Hz), 1.16 (d, 3H, −CH-CH_3, $^3J_{H-H}$ = 6.6 Hz), 1.46 (q, 2H, -CH_2-, $^3J_{H-H}$ = 7.1 Hz), 2.96 (br, 1H, NH), 3.32 (m, 1H, -CH-). ^{31}P NMR ($CDCl_3$, 298 K); $A_2A'B$ spin system, δ (ppm) −5.51 to −6.22 [PCl(NHR) and $2PCl_2$ groups not distinguished], −8.15 [PCl_2]. (The *sec*-butylamino group is a center of chirality and so the two PCl_2 groups are anisochrous.[33,34])

2d: Yield: 0.74 g, 43%. Anal. Calcd for $C_4H_{10}Cl_7N_5P_4$: C, 9.60; H, 2.02; N, 14.0%, M, 500.2. Found: C, 11.18; H, 2.12; N, 13.41%. ESI-MS (m/z): $[M-2H]^+$, 497.9. ^{1} H NMR ($CDCl_3$, 298 K); δ (ppm) 1.41 (d, 9H, −C-CH_3, $^4J_{H-H}$ = 1.6 Hz), 3.24 (d, 1H, NH, $^2J_{P-H}$ = 9.9 Hz). ^{31}P NMR ($CDCl_3$, 298 K); A_2MX spin system, δ (ppm) −9.81 [PCl(NHR)], −8.56 [PCl_2], −7.07 [$2PCl_2$], $^2J_{PCl(NHR)PCl2}$ = 37.0 Hz, $^2J_{PCl2PCl2}$ = 32.5 Hz.

Syntheses of Compounds 3a−c. Compound (**2a−c**) (1.00 g, 2 mmol) was dissolved in 1 mL of dry THF in a 50 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath, and NaH (60% oil suspension, 0.08 g, 2 mmol) in 3 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction was stirred for a further 2 h at room temperature and followed by TLC on silica gel plates using *n*-hexane−dichloromethane (3:1), which showed one new product. THF (10 mL) was added to the reaction mixture slurry in order to filter, and the mixture was stirred for a while. The reaction mixture was filtered; the solvent was removed under reduced pressure, and the crude product was subjected to column chromatography using *n*-hexane−dichloromethane (3:1) as the eluent. The products **3a−c** were isolated as white crystals from *n*-hexane−dichloromethane.

3a: Yield: 1.67 g, 90%, mp 198 °C. Anal. Calcd for $C_8H_{18}Cl_{12}N_{10}P_8$: C, 10.36; H, 1.96; N, 15.10%, M, 927.5. Found: C, 10.87; H, 2.03; N, 14.95%. MALDI-TOF-MS (m/z): $[M]^+$, 927.3. ^{1} H NMR ($CDCl_3$, 298 K); δ (ppm) 0.88 (t, 6H, -CH_3, $^3J_{H-H}$ = 7.4 Hz), 1.27 (m, 4H, CH_3-CH_2-, $^3J_{H-H}$ = 7.4 Hz), 1.81 (quintet, 4H, $N-CH_2-CH_2$-, $^3J_{H-H}$ = 8.0 Hz), 3.49 (m, 4H, $N-CH_2$-). ^{31}P NMR ($CDCl_3$, 298 K); $A_2A_2'B_2B_2'$ spin system, δ (ppm) −9.61[PCl_2], −7.44[PNCl], $^2J_{P(NCl)PCl2}$ = 14.2 Hz, $^2J_{P(NCl)P(NCl)}$ = 8.8 Hz

3b: Yield: 1.63 g, 88%, mp 225 °C. Anal. Calcd for $C_8H_{18}Cl_{12}N_{10}P_8$: C, 10.36; H, 1.96; N, 15.10%, M, 927.5. Found: C, 10.66; H, 2.10; N, 14.50%. MALDI-TOF-MS (m/z): $[M + H]^+$, 928.3. ^{1}H NMR ($CDCl_3$, 298 K); δ (ppm) 0.96 (d, 12H, $-CH_3$, $^3J_{H-H}$ = 6.8 Hz), 2.52 (m, 2H, $-CH-$,$^3J_{H-H}$ = 6.9 Hz), 3.43 (m, 4H, $-CH_2-$).^{31}P NMR ($CDCl_3$, 298 K); $A_2A_2'B_2B_2'$ spin system δ (ppm) −8.07 [PCl_2], −6.92 [PNCl], $^2J_{P(NCl)PCl2}$ = 11.7 Hz, $^2J_{P(NCl)P(NCl)}$ = 7.7 Hz

3c: Yield: 1.39 g, 75%, mp 247 °C. Anal. Calcd for $C_8H_{18}Cl_{12}N_{10}P_8$: C, 10.36; H, 1.96; N, 15.10%, M, 927.5. Found: C, 10.72; H, 2.02; N, 14.90%. MALDI-TOF-MS (m/z): $[M + H]^+$, 928.2. ^{1}H NMR ($CDCl_3$, 298 K); δ (ppm) 0.95 (t, 6H, $-CH_2-CH_3$, $^3J_{H-H}$ = 7.4 Hz), 1.23 (d, 6H, −CH-CH_3-, $^3J_{H-H}$ = 7.1 Hz), 1.61, 1.94 (m, 4H, -CH_2-), 3.97 (m, 2H, -CH-). ^{31}P NMR ($CDCl_3$, 298 K); $A_2B_2X_2X_2'$ spin system, δ (ppm) −3.02, −4.92 [PNCl], −13.29 [PCl_2], $^2J_{PNP}$ values could not be calculated accurately due to broad peaks.

Synthesis of Compound 4. Compound **2d** (1.00 g, 2 mmol) was dissolved in 1 mL of dry THF in a 50 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.08 g, 2 mmol) in 3 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction was stirred for a further 2h at room temperature and followed by TLC on silica gel plates using *n*-hexane-dichloromethane (3:1). A new product was not observed in the TLC analysis. THF (10 mL) was added to the reaction mixture slurry in order to filter and the mixture was stirred for a while. The reaction mixture was filtered; the solvent removed under reduced pressure and TLC analysis was done for mixture again. A little new product moving under of the starting compound on TLC was observed at this time. The crude product was subjected to column chromatography using *n*-hexane-dichloromethane (3:1) as the eluent. The unreacted starting compound **2d** was eluted from the column followed by compound **4**.

4: Yield: 0.19 g, 10%, mp 138 °C. Anal. Calcd for $C_8H_{20}Cl_{12}N_{10}OP_8$: C, 10.16; H, 2.13; N, 14.81%, M, 945.5. Found: C, 10.93; H, 2.22; N, 14.50%. ESI-MS (m/z): $[M - 2H]^+$, 942.9.

^{1}H NMR ($CDCl_3$, 298 K); δ (ppm) 1.41 (s, 18H, -CH_3), 3.23 (br, 2H, NH). ^{31}P NMR ($CDCl_3$, 298 K); $A_2A'_2BB'XX'$ spin system, δ (ppm) −6.95 to −7.82 [PNCl] and [$2PCl_2$], −21.22 [PNO]. $^2J_{PNP}$ values could not be calculated accurately due to broad peaks.

RESULT AND DISCUSSION

Synthesis and Characterization of the Reaction Products by ^{1}H and ^{31}P NMR Spectroscopy. The reaction mixtures were investigated by TLC and proton-decoupled ^{31}P NMR spectroscopy, and the structures of the isolated products were determined by elemental analysis, MS, and ^{1}H and ^{31}P NMR spectroscopy. All the analytical information is provided in the synthesis section for each new compound.

The mono amino cyclotetraphosphazene derivatives [$N_4P_4Cl_7$(NHR); R = *n*-butyl, *i*-butyl, *sec*-butyl, and *t*-butyl (**2a−d**)] were prepared from the reaction of octachlorocyclotetraphosphazene (tetramer) with butyl amines in the presence of triethylamine at 1:0.8 mol ratio in THF at room temperature for 4 h. The compounds **2a-d**, having mono butylamino group in the side chain, were reacted directly with sodium hydride in a 1:1 mol ratio in THF at room temperature for 2h under an argon atmosphere. The deprotonation reaction of compounds **2a**, **2b**, and **2c** resulted in the formation of a new class of tricyclic compounds (**3a−c**) having a 16-membered

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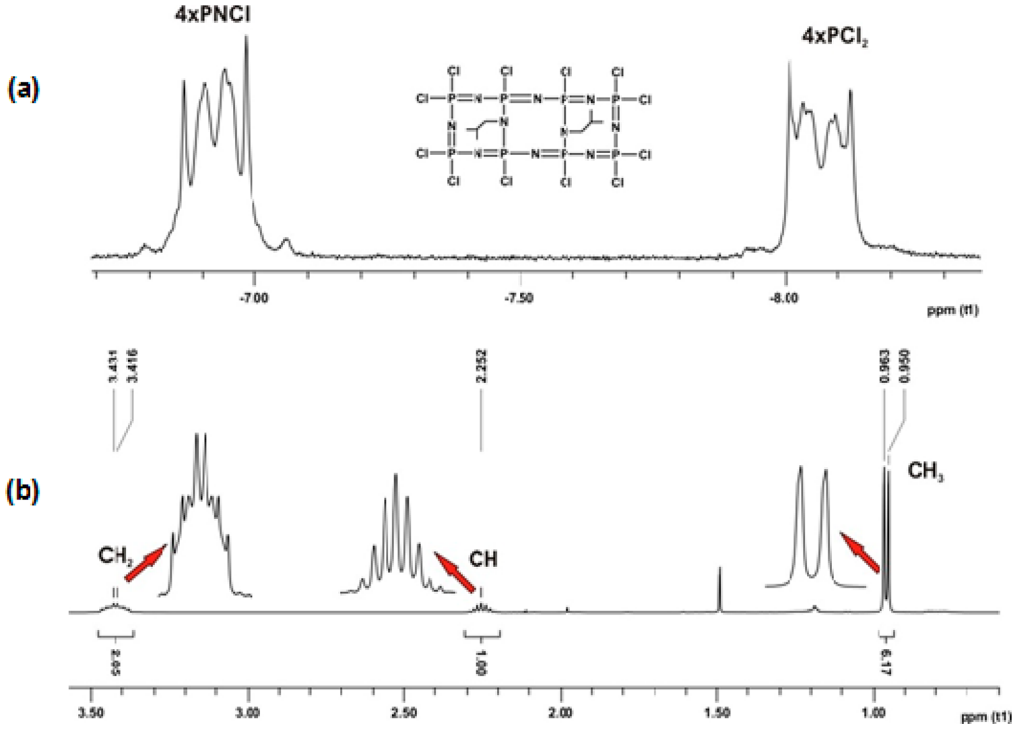

Figure 1. (a) Proton-decoupled ^{31}P NMR spectrum of compound **3b** (b) ^{1}H NMR spectrum of compound **3b**.

Table 1. X-ray Crystallographic Data and Refinement Parameters for Compounds 3b, 3c, and 4

compound	**3b**	**3c**	**4**
empirical formula	$C_8H_{18}Cl_{12}N_{10}P_8$	$C_8H_{18}Cl_{12}N_{10}P_8$	$C_8H_{20}Cl_{12}N_{10}OP_8$
fw	927.48	927.48	945.50
temp (K)	150(2)	150(2)	120(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	*P*1	*P*21/*n*	*P*21/*c*
a (Å)	8.4525(9)	10.0452(4)	23.3284(10)
b (Å)	10.6253(11)	11.8944(5)	8.6540(4)
c (Å)	11.0201(12)	13.9454(6)	19.2089(9)
α (deg)	109.534(5)°		
β (deg)	108.377(5)°	96.701(2)°	114.088(2)°
γ (deg)	105.271(5)°		
vol (Å^3)	806.43(15)	1654.84(12)	3540.3(3)
Z	1	2	4
density (calcd, mg/m^3)	1.910	1.861	1.774
absorption coefficient (mm^{-1})	1.453	1.416	1.327
F(000)	460	920	1880
cryst size (mm^3)	0.09 × 0.26 × 0.28	0.08 × 0.24 × 0.26	0.09 × 0.15 × 0.20
θ_{max} (deg)	25.03	24.99	28.36
reflns collected	11 304	23 186	61 281
independent reflns	2833	2914	8841
R_{int}(merging *R* value)	0.0330	0.0296	0.0464
data/restraints/params	2833/0/174	2914/4/192	8841/8/365
R (F^2\>2σF^2)	0.0201	0.0222	0.0442
wR (all data)	0.0556	0.0582	0.1067
goodness-of-fit on F^2	1.096	1.051	1.027
$\Delta\rho$ max/min (eÅ^{-3})	0.332/−0.349	0.389/−0.271	1.244 /−1.024

cyclooctaphosphazene (P_8N_8) ring fused ring assembly bridged by two aminoalkyl groups (Scheme 2). The new compounds are formed in high yields, are stable, and do not react with added gaseous HCl. Compound **2d** underwent hydrolysis to a give an oxo bridged dimer rather than the fused ring assembly reaction under the deprotonation conditions.

The proton-decoupled ^{31}P NMR spectra of the compounds **2a**, **2b**, and **2d** exhibit AM_2X (A_2MX) type spin systems due to three different phosphorus environments within the molecule as expected. Doublets of doublets for two equivalent PCl_2 groups at ca. −5.37 ppm (for **2a**), −5.45 ppm (for **2b**), −7.07 ppm (for **2d**) and triplets for another PCl_2 group at ca. −8.00

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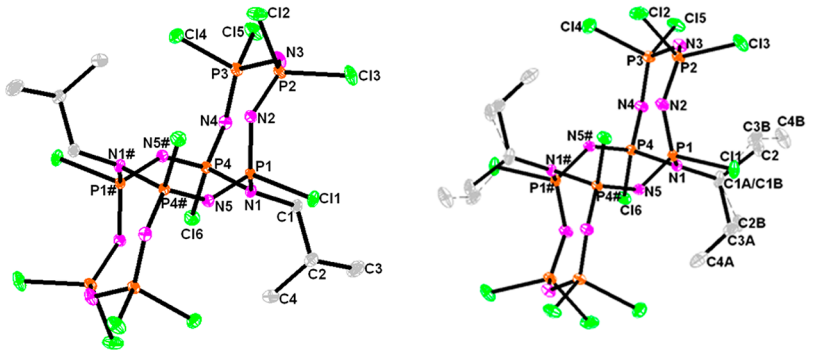

Figure 2. Crystal structures of **3b** and **3c** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level at 150 K. The hydrogen atoms have been omitted for clarity. In compound **3c**, the alkyl groups have two orientations which are labeled as A and B, C1A has *R* chirality, and C1B has *S* chirality [symmetry code (#) is $-x, -y + 1, -z + 1$ for **3b** and $-x + 2, -y + 1, -z + 1$ for **3c**].

ppm (for **2a**), −7.97 ppm (for **2b**), −8.56 ppm (for **2d**) and PCl(NHR) group at ca. −3.54 ppm (for **2a**), −3.18 ppm (for **2b**), −9.81 ppm (for **2d**) are observed. The proton coupled signals of PCl(NHR) groups are observed as multiplets, whereas the signals of the PCl_2 groups remain unchanged. The proton-decoupled ^{31}P NMR spectrum of **2c** has an $A_2A'B$ spin system. The signals of two PCl_2 groups and PCl(NHR) group are observed between −5.51 and −6.22 ppm as multiplets and the signals at ca. −8.15 ppm belong to the other PCl_2 group.

The proton-decoupled ^{31}P NMR spectra of compounds **3a** and **3b** consist of two multiplets corresponding to four PNCl group and four PCl_2 group ($A_2A_2'B_2B_2'$ spin system), whereas those for **3c**, which contains a chiral center in each alkyl chain, consists of three sets of multiplets ($A_2B_2X_2X_2'$ spin system) corresponding to meso and racemic diastereoisomers. The proton-decoupled ^{31}P NMR spectrum of compound **3b** is given as an example in Figure 1a. The proton-decoupled ^{31}P NMR spectrum of compound **4** exhibits a complex $A_2A'_2BB'XX'$ type of spin system. The MS data indicates that compound **4** is a dicyclotetraphosphazene derivative having 12 *Cl* atoms (from the number of *Cl* isotope peaks and the relative intensity of each peak) and the ^{31}P NMR spectra indicate that they are symmetrical. The P−O−P bridged cyclophosphazene structure was confirmed by X-ray crystallography.

The -NH- protons appeared between 2.96 and 3.24 ppm in the ^1H NMR spectra of compounds **2a-d.** In general, the ^1H NMR spectra of compounds **3a−c** are similar to compounds **2a-c,** with the exception of the absence of the -NH- protons are as expected for **3a-c,** the CH_3 protons were observed between 0.88 and 0.96 ppm and the protons which are adjacent to nitrogen atoms are observed between 3.43 and 3.97 ppm. Although the ^{31}P NMR spectra are clean, there is ^1H NMR evidence of low level impurities in **2a−d**. These are most like due to residual solvent in the oily products. This is also reflected in the elemental analyses. The ^1H NMR spectrum of **3b** is shown as an example in Figure 1b. The ^1H NMR spectrum of compound **4** is very similar to compound **2d.** The CH_3 protons were observed at 1.41 ppm and the NH proton at 3.23 ppm.

Characterization of Compounds by X-ray Crystallography. The molecular structures of compounds **3b**, **3c**, and **4** were established by X-ray structure analysis. The appropriate crystallographic data, selected bond and conformational parameters are summarized in Table 1 and Tables S1−S3, respectively. The molecular structure of compound **3a** was also confirmed by X-ray analysis, but the crystal structure could not be fully elucidated due to crystallographic problems which were probably due to poor crystal quality.

Compound **3b** has a triclinic system, space group *P*1, and compound **3c** has a monoclinic system, space group $P2_1/n$, with molecules in both structures sitting on inversion centers (Figure 2). The molecular structures show that both compounds **3b** and **3c** (Figure 2) contain a 16-membered cyclooctaphosphazene ring (P_8N_8) bridged by two P−N−P moieties to form a novel type of tricyclic compound containing three fused 8-membered rings. The cyclooctaphosphazene rings of both molecules have four equivalent stereogenic centers [P1(*R*), P4(*S*), P1#(*S*) and P4#(*R*)], but the molecules are meso due to the center of inversion. The P−N bond lengths of the cyclooctaphosphazene are in the range of 1.554(2)−1.582(2)Å, which are similar to those observed for previous cyclooctaphosphazene derivatives (Table S1) and indicate equivalent electron distribution in the cyclooctaphosphazene ring.[35−38] On the other hand, the P−N bond lengths of the bridges are in the range of 1.682(2)−1.687(1) Å (Table S1), indicating the single bond character of P−N−P bridges.

In these structures, the 16-membered cyclooctaphosphazene rings have similar chair conformations, as shown for compound **3b** in Figure S1. The phosphorus atoms are almost coplanar in each 8-membered internal and terminal rings and the nitrogen atoms are displaced alternatively above (+) and below (−) the main plane of the phosphorus atoms. The deviation of each nitrogen atom is given in Table S2. Based on the main plane of the phosphorus atoms, two 8-membered terminal rings are completely parallel, owing to inversion symmetry of the structures, and the internal 8-membered ring is located at an angle of 63.46° to these terminal rings for **3b** and 63.77° for **3c** (Figure S1). The chair conformation is consolidated by narrowing of the N−P−N angles of the phosphorus atoms bounded to the bridgehead nitrogen atoms, P1 and P4; the average N−P−N angle is 114.80 (±0.49)° for these phosphorus atoms, whereas the average of the other three is 121.14 (±0.63)° (Table S1). Similarly, the P−N−P bond angles of the cyclooctaphosphazene ring vary from 127.6(1)° to 139.4(1)° reflecting relief of the strain in the structure. The P−N−P bond angle belonging to the bridging nitrogen (N1) atom is 115.0(8)° in **3b** and 114.7(9)° in **3c**, and the sum of the bond angles around these nitrogen (N1) atoms is 354.25° for

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3b and 359.06° for **3c**, indicating their trigonal planar geometry.

The molecular structure of compound **4** (Figure 3) confirmed that it is the unexpected P−O−P bridged

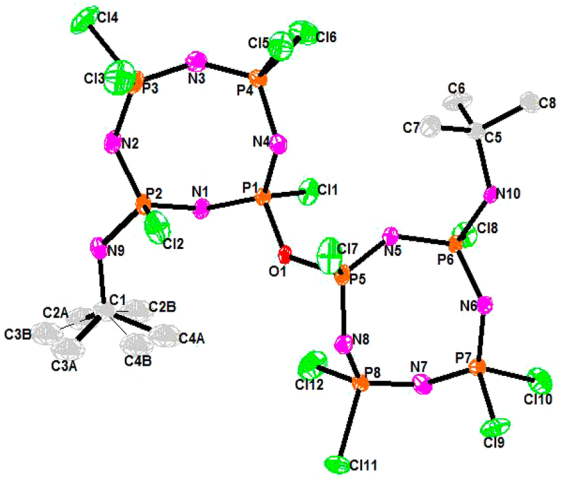


Figure 3. Crystal structure of **4** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level at 150 K. The methyl groups of the one *t*-butyl have two orientations which are labeled as A and B. The hydrogen atoms have been omitted for clarity.

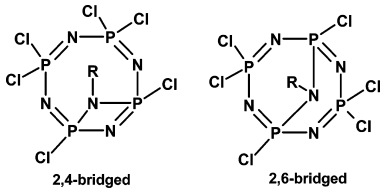
compound, which has been synthesized for the first time in the cyclotetraphosphazene system. One cyclotetraphosphazene ring has a slightly twisted boat conformation, while the other one has a flattened chair conformation. Two cyclotetraphosphazene rings are bridged via an oxygen atom from phosphorus atoms adjacent to the P(NHR) groups. The P−O−P bond angle [135.06(13)°] and the average P−O bond length [1.594(±0.003)Å] are similar to values for P−O−P bridged cyclotriphosphazene derivatives in the literature (Table S3).[25] Compound **4** has four stereogenic centers as two pairs of two different centers of chirality but the molecules are meso [first equivalent centers P1(*R*), P5(*S*) and second equivalent centers P2(*R*), P6(*S*)]. The crystal has a centrosymmetric space gruup, $P2_1/c$.

It is likely that the P−O−P bridged compound **4** is hydrolysis product resulting from trace amounts of moisture in the solvent (tetrahydrofuran), and a proposed reaction mechanism is given in the next section.

Formation of the Cyclooctaphosphazenes. On the basis of our previous studies on deprotonation reactions of cyclotriphosphazenes,[24−26] the formation of three possible isomers (spiro bridged; 2,4-ansa bridged; 2,6-ansa bridged) are also expected for the tetrameric analogues (Scheme S1). On the other hand, it has been demonstrated previously that the deprotonation of secondary amine derivatives of cyclotetraphosphazenes leads to intramolecular displacement of a chloride and formation of 2,6 bridged bicyclic compounds.[39−46] In this case, deprotonation reaction of cyclotetraphosphazenes containing exosecondary amino group such as **2a−d** can follow inter or intramolecular reaction pathways so the question remains how did compounds **3a−c** occur?

Intramolecular nucleophilic reactions of 2,6-diamino-substituted and 2,4,6,8-tetra-amino-substituted cyclotetraphosphazenes gave only the 2,6-bridged bicyclic phosphazenes.[39−46] The 2,4-bridged bicyclic phosphazenes have not previously been observed. However, compounds **2a−d** having a secondary amine group can give either a 2,4-bridged or the 2,6-bridged compound in an intramolecular deprotonation reaction (Scheme 4).

Scheme 4. 2,4 and 2,6-Bridged Bicyclophosphazenes



A proton abstraction/chloride ion elimination process is reasonable in the first step followed by the 2,4-bridge formation via an intramolecular reaction. This gives highly strained four-membered monophosphazenes followed by formation the P_8N_8 rings, which are stabilized by the two N−P−N bridged by an intermolecular reaction in the second step (Scheme 5). Alternatively, the intermolecular reaction of the 2,4 bridged species may be concerted but will still be driven by the charge distribution shown in Scheme 5. In any case, it is difficult to envision any process by which a 2,6 bridged intermediate could lead to the fused ring structures of **3** since there are no 2,6 linkages observed.

Another possibility would be the direct reaction of the deprotonated species with the starting material; however, the product of this process would have a structure which is different from the observed structure of **3** (Scheme 6 and Scheme S1).

According to the literature, bicyclic phosphazenes (Scheme 4) are not formed when the exosecondary amino group is α-branced (e.g., R = Pr^i, Ph).[41] In this study, the deprotonation reaction of *n*-butyl, *i*-butyl, *sec*-butyl derivative of the cyclotetraphosphazenes **2a−c** led to formation of cyclooctaphosphazenes (**3a−c**) by a mechanism proceeding through an intermediate bicyclic phosphazene. The deprotonation reaction of *t*-butyl derivative of cyclotetraphosphazene (**2d**) did not give the fused ring cyclooctaphosphazene compound presumably because of steric effects of the *t*-butyl group. The reaction medium is very basic and the P−O−P bridged compound (**4**) was obtained as a result of a hydrolysis reaction associated with advantageous moisture in the solvent tetrahydrofuran. Compound **4** is the first examples of P−O−P bridged cyclotetraphosphazene. The proposed hydrolysis reaction mechanism (S_N2) for the formation of P−O−P bridged compound (**4**) is shown in Scheme 7. However, the hydrolysis reactions of similar derivatives of cyclotriphosphazenes take place by a S_N1 mechanism.[25]

Furthermore, when sodium hydride was added to a 1:1 mol ratio mixture of mono *i*-butylamino derivative of cyclotriphosphazene with a mono substituted *i*-butylamino derivative of cyclotetraphosphazene (**2b**), the exclusive formation of the spiro bridged bis cyclotriphosphazene and compound **3b** was observed. The ^{31}P NMR spectrum (Figure S2), and TLC investigations did not show evidence for any additional products. This result indicates that the reaction is very selective for mono amino cyclotri- and tetraphosphazene derivatives and strongly suggests an intramolecular process in the fused ring formation.

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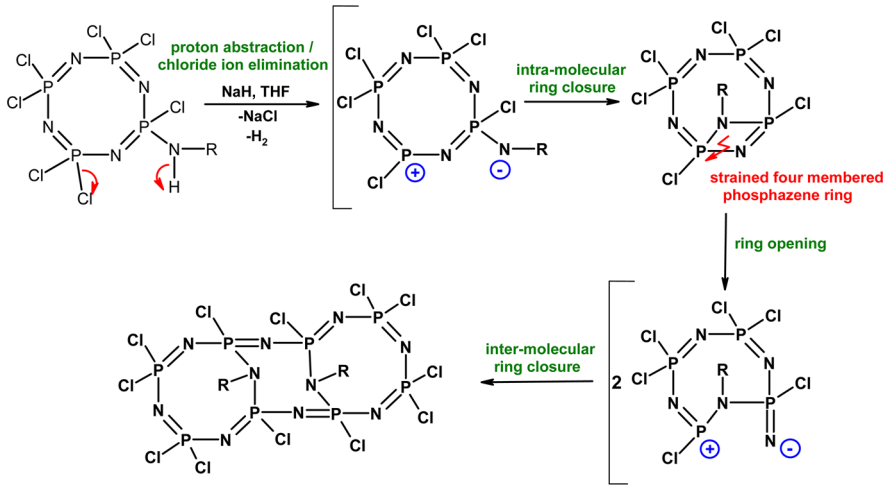
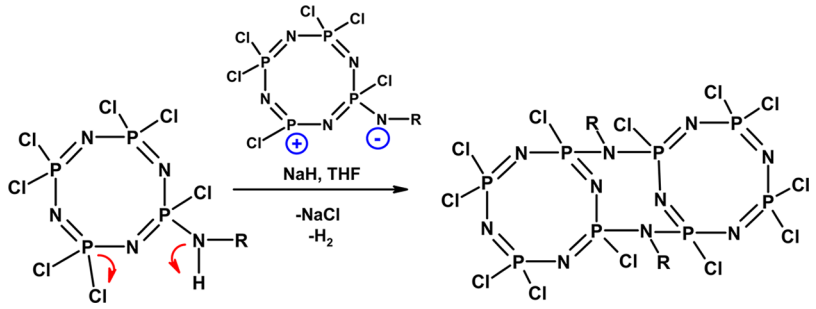
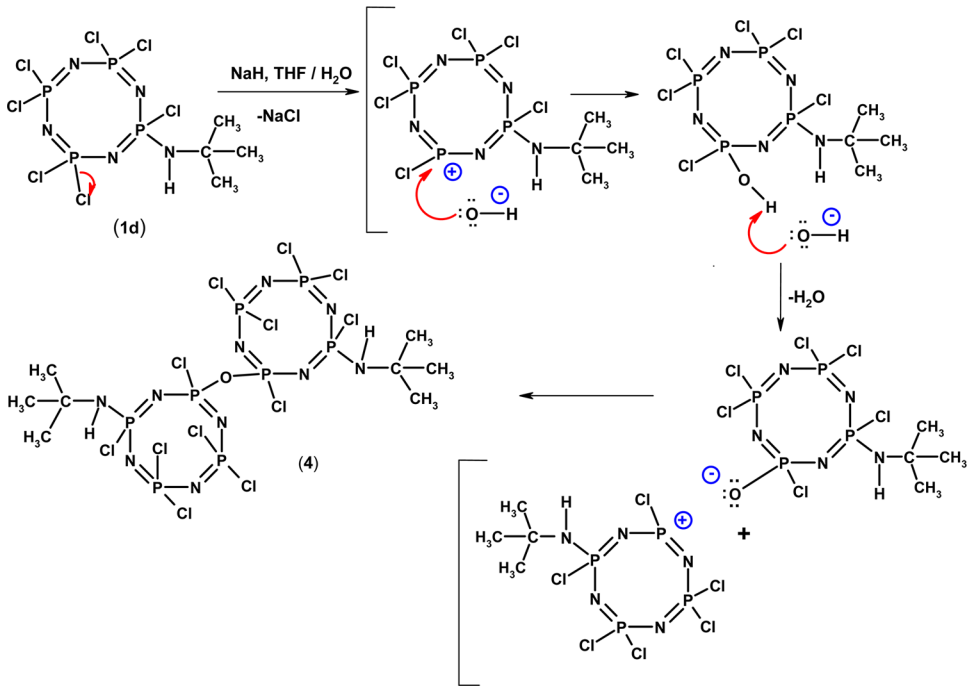
Scheme 5. Proposed Mechanism for Formation of Compounds 3a−c



Scheme 6. Alternative Pathway



Scheme 7. Proposed Reaction Mechanism for Formation of P−O−P Bridged Compound 4



CONCLUSION

The new fused ring cyclooctaphosphazene compounds are formed in high yield (90% for **3a**, 88% for **3b**, and 75% for **3c**) and they are very stable (mp: 198 °C for **3a**, 225 °C for **3b**, and 247 °C for **3c**). They have four PCl_2 groups at the corners of a planar rectangle and four PCl groups at the middle, which make them potential precursors for preparation of macromolecular and supramolecular systems with different structural and mechanical properties. Deprotonation reactions bring a new

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perspective to the chemistry of cyclophosphazenes, which are important heterocyclic inorganic ring systems, and the syntheses of new stable bridged cyclophosphazene compounds have been achieved. It has been demonstrated that higher heterocyclic systems can be synthesized via deprotonation reactions depending on the size of the cyclophosphazene ring precursor, and these results open up a general synthetic route for new heterocyclic structures.

Furthermore, these new type of cyclooctaphosphazenes (**3a**–**c**) have 12 available reactive phosphorus-chlorine bonds allowing for a wide spectrum of available reactions. This property is being investigated by reactions with various di- and monofunctional reagents in order to explore the possibility that the new compounds can be used as precursors in the synthesis of macromolecular and supramolecular systems. This work along with the recently characterized large ring traditional chlorophosphazenes[47] indicates that significant advances in the chemistry of macrocylic phosphazenes may be expected.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Bond lengths, bond angles, conformation patterns; depiction of possible structures; NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Ozay, H.; Ozay, O. *Colloids Surf., A* **2014**, *450*, 99–105.
(2) Sun, J.; Yu, Z.; Wang, X.; Wu, D. *ACS Sustainable Chem. Eng.* **2014**, *2*, 231–238.
(3) Davarcı, D.; Beşli, S.; Demirbaş, E. *Liq. Cryst.* **2013**, *40* (5), 624–631.
(4) He, Q.; Dai, H.; Tan, X.; Cheng, X.; Liu, F.; Tschierskec, C. *J. Mater. Chem. C* **2013**, *1* (43), 7148–7154.
(5) Keller, M. A.; Saba, C. S. *Anal. Chem.* **1996**, *68* (19), 3489–3492.
(6) Inoue, K.; Yamauchi, T.; Itoh, T.; Ihara, E. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17* (2), 367–375.
(7) Klein, R. J.; Welna, D. T.; Weikel, A. L.; Allcock, H. R.; Runt, J. *Macromolecules* **2007**, *40*, 3990–3995.
(8) Chandrasekhar, V.; Thilagar, P.; Pandian, B. M. *Coord. Chem. Rev.* **2007**, *251*, 1045–1074.
(9) Li, X.; Jiang, F.; Chen, L.; Wu, M.; Chen, Q.; Bu, Y.; Hong, M. *Dalton Trans.* **2012**, *41* (46), 14038–14041.
(10) Allcock, H. R. *Chemistry and Application of Polyphosphazenes*; Wiley-Interscience: Hoboken, NJ, 2003.
(11) *Applicative Aspects of Cyclophosphazenes*; Gleria, M., De Jaeger, R., Eds.; Nova Science Publishers: New York, 2004.
(12) Kagit, R.; Yildirim, M.; Ozay, O.; Yesilot, S.; Ozay, H. *Inorg. Chem.* **2014**, *53* (4), 2144–2151.
(13) Uslu, A.; Güvenaltın, Ş. *Dalton Trans.* **2010**, *39* (44), 10685–10691.
(14) Çiftçi, G. Y.; Eçik, E. T.; Yıldırım, T.; Bilgin, K.; Şenkuytu, E.; Yuksel, F.; Uludağ, Y.; Kılıç, A. *Tetrahedron* **2013**, *69*, 1454–1461.
(15) Alidağı, H. A.; Gırgıç, Ö.M.; Zorlu, Y.; Hacıvelioğlu, F.; Çelik, S. Ü.; Bozkurt, A.; Kılıç, A.; Yesilot, S. *Polymer* **2013**, *54*, 2250–2256.
(16) Richards, P. I.; Steiner, A. *Inorg. Chem.* **2005**, *44* (2), 275–281.
(17) Benson, M. A.; Ledger, J.; Steiner, A. *Chem. Commun.* **2007**, 3823–3825.
(18) Lawson, G. T.; Rivals, F.; Tascher, M.; Jacob, C.; Bickley, J. F.; Steiner, A. *Chem. Commun.* **2000**, 341–342.
(19) Okutan, E.; Çoşut, B.; Kayıran, S. B.; Durmuş, M.; Kılıç, A.; Yeşilot, S. *Polyhedron* **2014**, *67*, 344–350.
(20) Çiftçi, G. Y.; Şenkuytu, E.; Yuksel, F.; Kılıç, A. *Polyhedron* **2014**, *77*, 1–9.
(21) Chandrasekhar, V.; Krishnan, V. *Adv. Inorg. Chem.* **2002**, *53*, 159–211.
(22) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119–135.
(23) İbişoğlu, H.; Beşli, S.; Yuksel, F.; Ün, İ.; Kılıç, A. *Inorg. Chim. Acta* **2014**, *409*, 216–226.
(24) Beşli, S.; Coles, S. J.; Davies, D. B.; Erkovan, A. O.; Hursthouse, M. B.; Kılıç, A. *Inorg. Chem.* **2008**, *47* (12), 5042–5044.
(25) Beşli, S.; Coles, S. J.; Davies, D. B.; Kılıç, A.; Shaw, R. A. *Dalton Trans.* **2011**, *40*, 5307–5315.
(26) Beşli, S.; Yuksel, F.; Davies, D. B.; Kılıç, A. *Inorg. Chem.* **2012**, *51*, 6434–6436.
(27) *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, 2005.
(28) *Bruker APEX2, version 2011.4-1*; Bruker AXS Inc.: Madison, Wisconsin, 2008.
(29) Sheldrick, G. M. *SHELXS97*; University of Göttingen: Göttingen, Germany, 1997.
(30) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36* (1), 7–13.
(31) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39* (3), 453–457.
(32) Brandenburg, K. *DIAMOND 3.1 for Windows*; Crystal Impact GbR: Bonn, Germany, 2006.
(33) Vicente, V.; Fruchier, A.; Cristeau, H. J. *Magn. Reson. Chem.* **2003**, *41* (3), 183–193.
(34) Bilge, S.; Demiriz, S.; Okumus, A.; Kilic, Z.; Tercan, B.; Hokelek, T.; Buyukgungor, O. *Inorg. Chem.* **2006**, *45* (21), 8755–8767.
(35) Paddock, N. L.; Trotter, J.; Whitlow, S. H. *J. Chem. Soc. A* **1968**, *9*, 2227–2236.
(36) Calhoun, H. P.; Paddock, N. L.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1976**, *1*, 38–42.
(37) Oakley, R. T.; Paddock, N. L.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1977**, *55* (13), 2530–2533.
(38) Chaplin, A. B.; Harrison, J. A.; Dyson, P. J. *Inorg. Chem.* **2005**, *44*, 8407–8417.
(39) Cameron, T. S.; Cordes, R. E.; Vincent, B. R. *Acta Crystallogr.* **1986**, *C42*, 1242–4246.
(40) Krishnamurthy, S. S.; VasudevaMurthy, A. R.; Shaw, R. A.; Woods, M. *J. Indian Inst. Sci.* **1979**, *61* (2), 57–83.
(41) Krishnamurthy, S. S.; Ramachandran, K.; Sau, A. C.; Shaw, R. A. *Inorg. Chem.* **1979**, *18* (7), 2010–2014.
(42) Narayanaswamy, P. Y.; Dhathathreyan, K. S.; Krishnamurthy, S. S. *Inorg. Chem.* **1985**, *24* (5), 640–642.
(43) Öztürk, L.; Işıklan, M.; Kılıç, Z.; Hökelek, T. *Acta Crystallogr.* **2002**, *C58*, o80–o83.
(44) Işıklan, M.; Kılıç, Z.; Akduran, N.; Hökelek, T. *J. Mol. Struct.* **2003**, *660*, 167–179.
(45) Contractor, S. R.; Kılıç, Z.; Shaw, R. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2023–2029.
(46) Krishnamurthy, S. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41* (3–4), 375–391.
(47) Bowers, D. J.; Wright, B. D.; Scionti, V.; Schultz, A.; Panzner, M. J.; Twum, E. B.; Li, L.- L.; Katzenmeyer, B. C.; Thome, B. S.; Rinaldi, P. L.; Wesdemiotis, C.; Youngs, W. J.; Tessier, C. A. *Inorg. Chem.* **2014**, *53* (17), 8874–8886.

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