Synthesis and characterization of alkyl- and acyl-substituted oxime–phosphazenes

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Abstract: Two oxime–cyclophosphazenes were prepared from the hexakis(4-formylphenoxy)cyclotriphosphazene (**2**) and hexakis(4-acetylphenoxy)cyclotriphosphazene (**8**). The reactions of these oximes with ethyl bromide, allyl bromide, propanoyl chloride, and acriloyl chloride were studied. Hexasubstituted compounds were obtained from the reactions of hexakis{4-[(hydroxyimino)methyl]phenoxy}cyclotriphosphazene (**3**) with ethyl bromide (**4**), allyl bromide (**5**), and propanoyl chloride (**6**), however, the oxime groups on **3** rearranged to nitrile (**7**) in the reaction of **3** with acriloyl chloride. Hexasubstituted compounds were also obtained from the reactions of hexakis{4-[(1)-*N*-hydroxyethaneimidoyl]phenoxy}cyclotriphosphazene (**9**) with allyl bromide (**11**) and propanoyl chloride (**12**). Tetra- and penta-substituted products were obtained from the reactions of **9** with ethyl bromide (**10**) and acriloyl chloride (**13**), respectively. All products were generally obtained in high yields. The structures of the compounds were defined by elemental analysis, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

Key words: hexachlorocyclotriphosphazene, phosphazene, oxime, oxime derivatives, oxime–phosphazenes.

Résumé : On a préparé deux oximes de cyclophosphazènes à partir de l'hexakis(4-formylphénoxy)cyclotriphosphazène (**2**) et de l'hexakis(4-acétylphénoxy)cyclotriphosphazène (**8**). On a étudié les réactions de ces oximes avec le bromure d'éthyle, le bromure d'allyle, le chlorure de propanoyle et le chlorure d'acryloyle. Les réactions de l'hexakis{4-[(hydroxyimino)méthyl]phénoxy}cyclotriphosphazène (**3**) avec le bromure d'éthyle (**4**), le bromure d'allyle (**5**) et le chlorure de propanoyle (**6**) conduit à la formation de produits hexasubstitués; toutefois, par réaction avec le chlorure d'acryloyle, les groupes oximes du composé **3** se réarrangent en nitrile (**7**). On a aussi obtenu des produits hexasubstitués lors des réactions de l'hexakis{4-[(1)-*N*-hydroxyéthaneimidoyl]phénoxy}cyclotriphosphazène (**9**) avec le bromure d'allyle (**11**) et le chlorure de propanoyle (**12**). Les réactions du composé **9** avec le bromure d'éthyle (**10**) et le chlorure d'acryloyle (**13**) conduisent respectivement à des produits tétra- et pentasubstitués. Tous les produits ont généralement été obtenus avec des rendements élevés. Les structures des composés ont été définies par des analyses chimiques et par les spectroscopies IR et RMN du ^{1}H, ^{13}C et ^{31}P.

Mots clés : hexachlorocyclotriphosphazène, phosphazène, oxime, dérivés d'oximes, oxime de phosphazène.

[Traduit par la Rédaction]

Introduction

The linear, cyclo- and poly-phosphazenes are the best known and most intensively studied phosphorus–nitrogen compounds (1–5). These compounds are reported to possess interesting biomedical properties and promising applications (6–9). Phosphazene polymers bearing flouroalkoxy or aryloxy groups stimulated considerable interest in the past as biologically inert, water insoluble polymers for blood vessel or heart valve construction (10). Cyclophosphazene derivatives, substituted with aziridine groups, were investigated as biomedical products because of their strong antitumor activity (11). Antimicrobial and biological effects of some phosphazenes on bacterial and yeast cells have been studied (12–14). On the other hand, it is known that phosphorus and nitrogen compounds are effective flame retardants for fibre materials (15). Some other applications include model compounds for polyphosphazenes, starting materials for the preparation of cyclolinear and (or) cyclomatrix phosphazene substrates, commercial polymers with carbon backbones containing pending cyclophosphazene groups, inorganic hydraulic fluids and lubricants, biologically important substrates such as anticancer agents, insect chemosterilants, pesticides and fertilizers, supports for catalysts, dyes, and crown ether phase-transfer catalysts for nucleophilic substitution reactions, core substrates for dendrimers, thermal initiators for anionic polymerization reactions, and photosensitive materials (16).

The literature contains reports on the synthesis of different linear, cyclic or polyphosphazenes (17–27). There are also a large number of literature reports on reactions of the functional groups on phosphazene substituents (10, 28). Typical of these include coupling reactions of trimeric phosphazene azides with aryloxy, alkoxy, and dialkylamino cosubstituents (29), *N*-vinylic phosphazenes with azodicarboxylic and

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acetylenic esters (30), polymers from 4-formylphenoxy (31, 32), from maleic (33), and from 3,4-methylenedioxyphenoxy substituents (34).

In this paper we have prepared oxime–cyclophosphazenes from hexakis(4-formylphenoxy)cyclotriphosphazene and hexakis(4-acetylphenoxy)cyclotriphosphazene, and studied their reactions with alkyl and acyl halides such as ethyl bromide, allyl bromide, propanoyl chloride, and acriloyl chloride.

Experimental

General remarks

Solvents and other liquids used in the experimental works were dried by conventional methods. Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) (**1**) was recrystallized from hexane. Other chemicals were used as purchased. Hexakis(4-formylphenoxy)cyclotriphosphazene (**2**) and hexakis(4-acetylphenoxy)cyclotriphosphazene (**8**) were prepared as described by Carriedo et al. (25). The reactions of ($N_3P_3Cl_6$) with the phenols were carried out under dry nitrogen.

The IR spectra were recorded on an ATI Unicam Mattson 1000 FT IR spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a Bruker DPX-300 spectrometer operating at 300.13, 75.46, and 121.49 MHz, respectively. The ^1H and ^{13}C NMR chemical shifts were measured using $SiMe_4$ as an internal standard and the ^{31}P chemical shifts were measured using 85% H_3PO_4 as an external standard. Chemical shifts downfield from the standard were assigned positive δ values. Microanalysis was carried out by a LECO 932 CHNS-O apparatus.

Synthesis of compound 2

A mixture of **1** (10.34 g, 29.74 mmol), 4-hydroxybenzaldehyde (22.05 g, 180.56 mmol), and K_2CO_3 (50.00 g, 361.76 mmol) was stirred in THF (250 mL) at 0 °C and then was reacted at ambient temperature for 48 h. The solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (4 × 75 mL). After the solvent was removed, a white solid (**2**) formed in 92% (23.57 g) yield.

Synthesis of compound 3

A mixture of **2** (20.00 g, 23.21 mmol) and hydroxylaminehydrochloride (10.00 g, 143.90 mmol) was refluxed in pyridine (15 mL) for 3 h. After the reaction was complete, the mixture was allowed to cool and was slowly poured into water (100 mL) and reprecipitated twice from water. The white solid (**3**) was washed with alcohol and dried at 50 °C in a vacuum. Yield: 83% (18.33 g).

Reaction of 3 with ethyl bromide

A solution of 0.40 mL (0.74 g, 6.79 mmol) ethyl bromide in acetone (10 mL) was slowly added dropwise to a stirred and cooled (0–5 °C) mixture of **3** (0.80 g, 0.84 mmol) and K_2CO_3 (2.00 g, 14.47 mmol) in acetone (30 mL). The reaction was carried out at room temperature for 1 h and then was refluxed for 24 h. After the reaction was complete, the mixture was slowly poured into water (50 mL) and reprecipitated twice from water. The white solid (**4**) was recrystallized from chloroform. Yield: 59% (0.55 g).

Reaction of 3 with allyl bromide

A solution of 0.50 mL (0.7 g, 5.77 mmol) allyl bromide in acetone (10 mL), **3** (0.80 g, 0.84 mmol), and K_2CO_3 (1.60 g, 11.57 mmol) in acetone (30 mL) was used for the preparation of **5** as for **4**. The reflux period was 48 h. The white solid (**5**) was recrystallized from alcohol. Yield: 84% (0.85 g).

Reaction of 3 with propanoyl chloride

A solution of 0.40 mL (0.42 g, 4.58 mmol) propanoyl chloride in acetone (10 mL), **3** (0.60 g, 0.63 mmol), and Et_3N (2 mL) in acetone (30 mL) was used for the preparation of **6** as for **4**. The reaction was carried out at room temperature for 12 h. The white solid (**6**) was recrystallized from alcohol. Yield: 74% (0.60 g).

Reaction of 3 with acriloyl chloride

A solution of 0.40 mL (0.44 g, 4.86 mmol) acriloyl chloride in acetone (10 mL), **3** (0.60 g, 0.63 mmol), and Et_3N (2 mL) in acetone (30 mL) was used for the preparation of **7** as for **4**. The reaction was carried out at room temperature for 12 h. The orange colour solid (**7**) was washed with alcohol. Yield: 94% (0.50 g).

Synthesis of compound 8

A mixture of **1** (7.00 g, 20.13 mmol), 4-hydroxyacetophenone (16.72 g, 122.80 mmol), and K_2CO_3 (34.00 g, 245.99 mmol) was refluxed in acetone (250 mL) for 3 h. The solvent was evaporated in vacuum and the residue was extracted with CH_2Cl_2 (4 × 75 mL). After the evaporation of the solvent in vacuum, a white solid (**8**) formed in 87% (16.50 g) yield.

Synthesis of compound 9

Hydroxylaminehydrochloride (4.50 g, 64.75 mmol) and **8** (10.00 g, 10.57 mmol) were used for the preparation of **9** as for **3**. After the reaction was complete, the mixture was allowed to cool and the mixture was slowly poured into water (100 mL) and reprecipitated twice from water. The white solid (**9**) was obtained in 99% (10.89 g) yield.

Reaction of 9 with ethyl bromide

A solution of 0.40 mL (0.59 g, 5.43 mmol) ethyl bromide in acetone (10 mL), **9** (0.60 g, 0.58 mmol), and K_2CO_3 (2.00 g, 14.47 mmol) in acetone (30 mL) was used for the preparation of **10** as for **4**. The oily product (**10**) was obtained and dried under vacuum for 48 h. Yield: 62% (0.41 g).

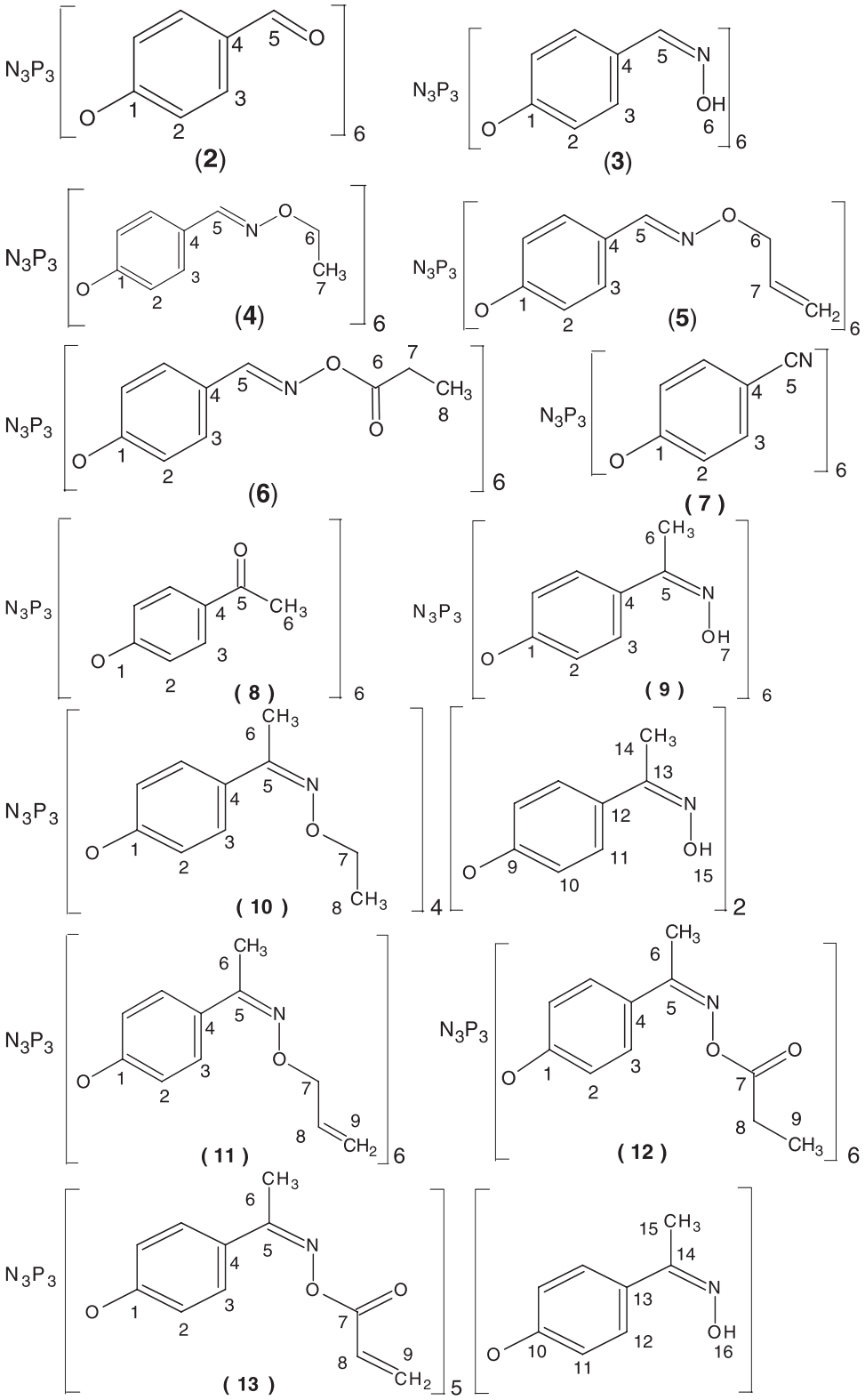
Reaction of 9 with allyl bromide

A solution of 0.40 mL (0.55 g, 4.56 mmol) allyl bromide in acetone (10 mL), **9** (0.60 g, 0.58 mmol), and K_2CO_3 (2.00 g, 14.47 mmol) in acetone (30 mL) was used for the preparation of **11** as for **4**. The reflux period was 48 h. The oily product (**11**) was obtained and dried under vacuum for 48 h. Yield: 89% (0.65 g).

Reaction of 9 with propanoyl chloride

A solution of 0.40 mL (0.42 g, 4.60 mmol) propanoyl chloride in acetone (10 mL), **9** (0.60 g, 0.58 mmol), and K_2CO_3 (2.00 g, 14.47 mmol) in acetone (30 mL) was used for the preparation of **12** as for **4**. The oily product (**12**) was

Scheme 1. The structures of compounds **2**–**13**.



obtained and dried under vacuum for 24 h. Yield: 89% (0.70 g).

Reaction of 9 with acriloyl chloride

A solution of 0.40 mL (0.44 g, 4.86 mmol) acriloyl chloride in acetone (10 mL), **9** (0.60 g, 0.58 mmol), and Et_3N (2 mL) in acetone (30 mL) was used for the preparation of **13** as for **4**. The reaction was carried out at room temperature for 24 h. The yellowish solid (**13**) was washed with alcohol three times. Yield: 59% (0.45 g).

Results and discussion

The reaction of **1** with 6 equiv. of 4-hydroxybenzaldehyde and 4-hydroxyacetophenone in the presence of K_2CO_3 in THF gave hexakis(4-formylphenoxy)cyclotriphosphazene (**2**) and hexakis(4-acetylphenoxy)cyclotriphosphazene (**8**). Oxime compounds hexakis{4-[(hydroxyimino)methyl]phenoxy}cyclotriphosphazene (**3**) and hexakis{4-[(1)-*N*-hydroxyethaneimidoyl]phenoxy}cyclotriphosphazene (**9**) were synthesized from the reactions of **2** and **8** with hydroxylaminehydrochloride in pyridine, respectively.

Hexasubstituted oxime derivatives were obtained from the reactions of oxime compound **3** with ethyl bromide, allyl bromide, and propanoyl chloride in acetone (in the presence of K_2CO_3 for ethyl and allyl bromide, of Et_3N for propanoyl and acriloyl chloride) via replacement of all the oxime protons with ethyl, allyl and propanoyl groups. However, the oxime groups on **3** rearranged to nitrile (**7**) in the reaction of **3** with acriloyl chloride via the dehydration of oximes (35, 36). Compound **7** was previously synthesized by Carriedo (25). $N_3P_3(OC_6H_4\text{-}CN)_6$ was directly obtained from the reaction of $N_3P_3Cl_6$ with 4-cyanophenol and characterized by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectra (25). The analysis results of **7** are in good accordance with the literature values (25). Similar compounds, $N_3P_3(OPh)_5(OC_6H_4\text{-}CN\text{-}p)$ and $N_3P_3(OC_6H_4\text{-}R\text{-}4)_5(OC_6H_4\text{-}CN\text{-}4)$ (R = H or *t*-Bu), were synthesized by Allcock et al. (37) and Carriedo et al. (38), respectively. Hexasubstituted derivatives were obtained from the reactions of **9** with allyl bromide and propanoyl chloride. Tetra- and penta-substituted products were obtained from the reactions of **9** with ethyl bromide and acriloyl chloride in acetone (in the presence of K_2CO_3 for ethyl bromide, of triethylamine for acriloyl chloride), respectively.

The structures of the compounds were defined by elemental analysis, IR, and ^1H, ^{13}C, and ^{31}P NMR spectroscopy (structures **2**–**13** are shown in Scheme 1). Physical properties and analytical data for **2**–**13** are given in Table 1. Compounds **2**–**13** were synthesized in high yields except **4**, **10**, and **13**. The solvents used for the purification of compounds **7**, **10**, and **11** could not be removed completely as observed by ^1H and ^{13}C NMR spectra. Thus, the presence of these trace amounts of solvent affect the elemental analysis, in particular the carbon value.

The characteristic stretching peaks in the IR spectra of the phosphazenes have been assigned as in Table 2. The P=N stretching vibrations, which are observed between 1173 and 1208 cm^{-1}, are characteristic of cyclophosphazenes. Compared to **1**, which appeared at 1218 cm^{-1}, these peaks are shifted to longer wavelengths for **2**–**13**. The OH stretching vibrations in the IR spectra of **3**, **9**, **10**, and **13** indicate the oxime compounds. While **3** and **9** are initial oximes, all hydrogen atoms of the OH groups of **10** and **13** could not be replaced by the alkyl and acyl substituents.

The NMR data for **2**–**13** are presented in Tables 3–5. The ^{31}P NMR shifts of **2**–**13** change between 8.05 and 17.21 ppm. Although there is only one peak in the ^{31}P NMR spectra of **1**, **2**, **4**, **5**, **7**, **8**, **10**, **12**, and **13** at 20.12, 8.33, 7.49, 9.49, 7.51, 8.05, 9.07, 8.80, and 8.73 ppm, respectively, two peaks, with very weak second signals, are observed at δ 17.21, 17.26, δ 8.33, 8.21, δ 9.04, 9.01, and δ 9.01 and 8.98 ppm for **3**, **6**, **9**, and **11**, respectively. It is assumed that the weak peaks due to the cyn and anti isomerism of the -C=N- groups. The effects of the cyn and anti isomerism are also observed in the ^{13}C NMR spectra of **3**, **6**, and **11** (Table 5). This data demoinstrates that compounds **3**, **6**, **9**, and **11** consist of a mixture of two isomers, but others have one isomer. Although there are the different phosphorus environments in the molecules of **10** and **13**, the main peak is observed as a singlet. It is understood that the phosphorus peaks are not affected by these changes because the substituted groups are far off the phosphorus atoms.

The ^1H and ^{13}C NMR data also confirm the structures of **2**–**13** (Scheme 1). In the ^1H NMR spectra (Table 4), the OH protons are observed at 10.17, 11.25, 11.30, and 11.25 ppm for **3**, **9**, **10**, and **13**, respectively. It is understood from the integral intensities that there are six OH protons in **3** and **9**, which are original oxime–phosphazenes, two OH protons in **10**, one OH proton in **13**. This observation for **10** and **13** indicates that alkyl or acyl groups have not replaced all OH protons in **3** and **9**. The aldehyde proton for **2** appears at

Table 1. Physical properties and analytical data for **2**–**13**.

Compound	Yield (%)	Atom	Found	Calcd.
2	92	C	58.52	58.55
		H	3.39	3.51
		N	4.51	4.88
3	83	C	53.43	53.00
		H	3.75	3.81
		N	12.98	13.25
4	59	C	58.16	57.91
		H	5.33	5.40
		N	11.02	11.26
5	84	C	60.10	60.45
		H	5.11	5.07
		N	10.40	10.57
6	74	C	56.21	55.95
		H	4.63	4.70
		N	9.21	9.79
7	94	C	58.29	59.80
		H	2.96	2.87
		N	13.33	14.94
8	87	C	60.93	60.96
		H	4.50	4.48
		N	4.40	4.44
9	99	C	55.67	55.66
		H	4.69	4.67
		N	11.98	12.17
10	62	C	56.42	58.58
		H	5.42	5.62
		N	9.48	10.98
11	89	C	60.76	62.11
		H	5.44	5.69
		N	8.92	9.88
12	89	C	57.27	57.77
		H	5.19	5.29
		N	8.38	9.10
13	59	C	58.28	57.93
		H	4.45	4.48
		N	9.27	9.65

Table 2. Characteristic IR vibrations (in cm^{-1}) for **2–13**.

Compound	ν_{OH}	$\nu_{C\text{-}Har.}$	$\nu_{C\text{-}Hal.}$	$\nu_{C=O}$	$\nu_{P=N}$	$\nu_{N\text{-}O\text{-}C}$	$\nu_{P\text{-}O\text{-}C}$
2	—	3040, 3100	2732, 2820	1706	1184	—	962
3	3340	3044, 3086	2903, 2980	—	1187	—	949
4	—	3059, 3100	2881, 2981	—	1179	1054	954
5	—	2976, 3087	2868, 2981	—	1179	1039	950
6	—	3060, 3097	2883, 2991	1764	1182	1070	973
7	—	3065, 3103	2951, 2997	—	1188	—	950
8	—	3067, 3105	2927, 3002	1685	1188	—	949
9	3460	3058, 3109	2913, 2981	—	1208	—	960
10	3309	2978, 3065	2886, 2931	—	1183	1048	956
11	—	2981, 3078	2864, 2920	—	1183	1036	959
12	—	3058, 3104	2937, 2981	1765	1186	1068	953
13	3410	3038, 3068	2860, 2927	1755	1173	1020	958

Table 3. ^{31}P NMR data for **1–13**.

Compound	Main compound (ppm)	Minor isomer (ppm)
1	20.12	—
2	8.33	—
3	17.21	17.26
4	7.49	—
5	9.49	—
6	8.33	8.21
7	7.51	—
8	8.05	—
9	9.04	9.01
10	9.07	—
11	9.01	8.98
12	8.80	—
13	8.73	—

Table 4. ^{1}H NMR data for **2–13**.

Compound	^{1}H NMR
2	7.10 (d) : H^2 ($^4J_{POCCH}$ = 8.50), 7.60 (d) : H^3 ($^5J_{POCCCH}$ = 8.56), 9.90 (s) : H^5; H^2:H3:H^5 = 2:2:1
3	6.86 (d) : H^2 ($^4J_{POCCH}$ = 8.45), 7.28(d) : H^3 ($^5J_{POCCCH}$ = 8.50), 7.96 (s) : H^5, 10.17 (s) : H^6, 7.20 : H^2 (is.), 7.77 : H^3 (is.); H^2:H^3:H^5:H^6 = 2:2:1:1
4	6.88 (d) : H^2 ($^4J_{POCCH}$ = 8.54), 7.38 (d) : H^3 ($^5J_{POCCCH}$ = 8.61), 7.97 (s) : H^5, 4.08 (q) : H^6, 1.16 (t) : H^7
5	6.88 (d) : H^2 ($^4J_{POCCH}$ = 8.47), 7.38 (d) : H^3 ($^5J_{POCCCH}$ = 8.55), 8.03 (s) : H^5, 4.55 (d) : H^6 (J = 5.59), 5.90 (m) : H^7, 5.10 (d) : H^8_{cis} (J = 10.23), 5.25 (d) : H^8_{trans} (J = 16.28)
6	7.05 (d) : H^2, 7.61 (d) : H^3, 8.60 (s) : H^5, 1.10 (t) : H^8, 2.50 (k): H^7
7	7.15 (d) : H^2, 7.85 (d) : H^3
8	7.05 (d) : H^2, 7.85 (d) : H^3, 2.45 (s) : H^6; H^2:H^3:H^6 = 2:2:3
9	6.85 (d) : H^2, 7.50 (d) : H^3, 2.10 (s) : H^6, 11.25 (s) : H^7; H^2:H^3:H^6:H^7 = 2:2:3:1
10	11.30 (s) : H^{15}, 6.90 : H_2, H^{10}, 7.55 : H_3, H^{11}, 4.15 (q) : H^7, 2.15 (s) : H^6, H^{14}, 1.25 (t) : H^8
11	6.88 (d) : H^2, 7.50 (d) : H^3, 6.00 (m) : H^8, 5.20 (d) : H^9_{cis}, 5.35 (d) : H^9_{trans}, 4.65 (d) : H^7, 2.15 (s) : H^6
12	7.00 (d) : H^2, 7.65 (d) : H^3, 2.60 (q) : H^8, 2.30 (s) : H^6, 1.15 (s) : H^9
13	11.25 (s) : H^{16}, 7.00 : H^2, H^{11}, 7.80 : H^3, H^{12}, 6.1 (d) : H^9_{cis}, 6.30–6.60 (m) : H^8, H^9_{trans}, 2.3 (s) : H^6, 2.10 (s) : H^{15}

Note: For numbering see Scheme 1; coupling constants J (Hz). Acetone-d (for **3–5**), $CDCl_3$-d (for **2**) and DMSO-d (for **6–13**) were used as solvents in NMR analyses. Isomer (is), singlet (s).

9.90 ppm. The azomethine protons for **3–6** are observed at 7.96 (H^5), 7.97 (H^5), 8.03 (H^5), and 8.60 (H^5) ppm, respectively. The aromatic protons for all the compounds appear between 6.85 and 7.85 ppm.

The detailed ^{13}C NMR spectral data are given in Table 5. The aldehyde carbon atom for **2** and ketone carbon atom for **8** are observed at 190.83 and 197.00 ppm, respectively, at the lowest downfield of the carbon atoms. Compared to **3**

Table 5. ^{13}C NMR data for **2–13**.

Compound	^{13}C NMR
2	121.60 : C^2, 131.40 : C^3, 134.14 : C^4, 154.80 : C^1, 190.83 : C^5
3	121.50 : C^2, 121.33 : C^2 (is), 129.00 : C^3, 129.37 : C^3 (is), 131.00 : C^4, 131.00 : C^4 (is), 148.19 : C_5, 151.70 : C^1
4	14.46 : C^7, 69.81 : C^6, 121.57 : C^2, 128.62 : C^3, 130.46 : C^4, 147.35 : C^5, 151.63 : C^1
5	151.63 : C^1, 147.93 : C^5, 134.92 : C^7, 130.20 : C^4, 128.72 : C^3, 121.57 : C^2, 117.33 : C^8, 75.29 : C^6
6	9.22 : C^8, 25.85 : C^7, 121.89 : C^2, 121.58 : C^2 (is), 128.13 : C^4, 130.27 : C^3, 134.93 : C^3 (is), 152.16 : C^1, 155.86 : C^5, 172.03 : C^6
7	152.88 : C^1, 135.07 : C^3, 121.99 : C^2, 118.85 : C^4, 109.37 : C^5
8	27.04 : C^6, 120.96 : C^2, 131.20 : C^3, 134.54 : C^4, 153.27 : C^1, 197.00 : C^5
9	11.90 : C^6, 120.93 : C^2, 127.36 : C^3, 134.64 : C^4, 150.39 : C^1, 152.51 : C^5
10	153.08 : C^{13}, 152.48 : C^5, 150.53 : C^9, 150.27 : C^1, 134.60 : C^{12}, 133.72 : C^4, 127.58 : C^{11}, 127.33 : C^3, 120.93 : C^2, C^{10}, 69.53 : C^7, 15.05 : C^8, 12.63 : C^{14}, 11.82 : C^6
11	12.69 : C^6, 74.88 : C^7, 74.57 : C^7 (is), 117.75 : C^9, 117.47 : C^9 (is), 120.99 : C^2, 120.53 : C^2 (is), 127.69 : C^3, 133.53 : C^4, 134.97 : C^8, 150.67 : C^1, 153.67 : C^5, 152.34 : C^5 (is)
12	9.29 : C^9, 14.19 : C^6, 26.12 : C^8, 121.16 : C^2, 128.94 : C^3, 132.25 : C^4, 151.68 : C^1, 161.91 : C^5, 171.88 : C^7
13	163.38 : C^7, 162.89 : C^5, 152.55 : C^{14}, 151.73 : C^1, 150.22 : C^{10}, 134.77 : C^4, 133.31 : C^{13}, 132.03 : C^9, 129.02 : C^3, 127.43 : C^8, 126.94 : C^{12}, 121.16 : C^2, 120.96 : C^{11}, 14.35 : C^6, 11.82 : C^{15}

Note: For numbering see Scheme 1. Acetone-*d* (for **3–5**), $CDCl_3$-*d* (for **2**), and DMSO-*d* (for **6–13**) were used as solvents in NMR analyses. Isomer (is).

and **9**, the azomethine carbon atoms in the substituted moiety of the molecules are shifted to the lower downfield for compound **6**, **11**, **12**, and **13**, except **4**, **5**, and **10** in which the alkyl groups release an electron to the molecule. But the azomethine resonances do not change or change very little in the nonsubstituted moieties of **10** and **13**. In addition, the ^{13}C NMR data clearly show that compound **10** is referred to as the geminal isomer. There are essentially two different sets of carbon atoms within the geminal structures, but three sets within the nongeminal structures for the tetrasubstituted cyclotriphosphazenes. The resonances of two sets of carbon atoms were observed in the ^{13}C NMR spectrum of **10**. These results indicate the geminal structure. A triplet and a doublet are expected in the ^{31}P NMR spectra of geminal structures for tetrasubstituted cyclotriphosphazene (**10**), but the main peak was observed as a singlet. These results show that the phosphorus signals are not affected from the binding groups because the substituents at the end of the molecule are far from the phosphorus atoms.

Conclusion

Hexasubstituted compounds were obtained from the reactions of hexakis{4-[(hydroxyimino)methyl]phenoxy}cyclotriphosphazene (**3**) with ethyl bromide, allyl bromide, and propanoyl chloride; however, the oxime groups on **3** rearranged to nitrile in the reaction of **3** with acriloyl chloride. Hexasubstituted compounds were also obtained from the reactions of hexakis{4-[(1)-*N*-hydroxyethaneimidoyl]phenoxy}cyclotriphosphazene (**9**) with allyl bromide and propanoyl chloride. The tetrasubstituted product, which is a geminal isomer, and pentasubstituted products were obtained from the reactions of **9** with ethyl bromide and acriloyl chloride, respectively.

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References

1. H.R. Allcock. Phosphorus–nitrogen compounds. Academic Press, New York. 1972.
2. C. Diaz, I. Izquierdo, F. Mendizabal, N. Yutronic. Inorg. Chim. Acta, **294**, 20 (1999).
3. A. Kılıç, S. Begeç, B. Çetinkaya, T. Hökelek, Z. Kılıç, N. Gündüz, and M. Yıldız. Heteroat. Chem. **7**, 249 (1996).
4. G.A. Carriedo, F.J.G. Alonso, P.G. Elipe, E. Brillas, and L. Julia. Org. Lett. **3**, 1625 (2001).
5. H.R. Allcock, C.T. Morrissey, W.K. Way, and N. Winograd. Chem. Mater. **8**, 2730 (1996).
6. H.R. Allcock. *In* Inorganic and organometallic polymers. *Edited by* H.R. Allcock, M. Zeldin, and K.J. Wynne. ACS Symposium Series 360. 1988. Chap. 19.
7. C.T. Laurencin, H.J. Koh, T.X. Neenan, H.R. Allcock, R. Langer. J. Biomed. Mater. Res. **21**, 1231 (1987).
8. H.R. Allcock, S.R. Pucher, R.J. Fitzpatrick, and K. Rashid. Biomaterials, **13**, 857 (1992).
9. G. Giavaresi, M. Tschon, V. Borsari, J.H. Daly, J.J. Liggat, M. Fini, V. Bonazzi, A. Nicolini, A. Carpi, M. Morra, C. Cassinelli, and R. Giardino. Biomedicine and Pharmacotherapy, **58**, 411 (2004).
10. G. Fantin, M. Fogagnolo, M. Gleria, A. Medici, F. Minto, and P. Pedrini. Tetrahedron, **52**, 9535 (1996).
11. K. Brandt, R. Kruszynski, T.J. Bartczak, and I.P. Czomperlik. Inorg. Chim. Acta, **322**, 138 (2001).
12. A.I. Ozturk, O. Yılmaz, S. Kırbag, and M. Arslan. Cell. Biochem. Funct. **18**, 117 (2000).
13. V. Konar, O.Yılmaz, A.I. Ozturk, S. Kırbag, and M. Arslan. Bioorg. Chem. **28**, 214 (2000).
14. O. Yılmaz, F. Aslan, A.I. Ozturk, N. Vanlı, S. Kırbag, and M. Arslan. Bioorg. Chem. **30**, 303 (2002).
15. C.W. Allen. J. Fire Sci. **11**, 320 (1993).
16. M. Gleria and R.D. Jaeger. J. Inorg. Organomet. Polym. **11**, 1(2001).
17. M.T.R. Laguna, M.P. Tarazona, G.A. Carriedo, F.J.G. Alonso, J.I. Fidalgo, and E. Saiz. Macromolecules, **35**, 7505 (2002).
18. E. Çil, M. Arslan, F. Aslan, and A.I. Ozturk. Phosphorus Sulfur Silicon Relat. Elem. **178**, 1037 (2003).
19. A.I. Ozturk, F. Aslan, E. Cil, M. Arslan, and A. Kılıç. Phosphorus Sulfur Silicon Relat. Elem. **178**, 2097 (2003).

20. M. Arslan, F. Aslan, and A.I. Ozturk. Heteroat. Chem. **14**, 138 (2003).
21. F. Aslan, A.I. Ozturk, and M. Arslan. Heteroat. Chem. **14**, 413 (2003).
22. C.V. Diaz and I.G. Izquierdo. Polyhedron, **18**, 1479 (1999).
23. R. Bertani, G. Facchin, and M. Gleria. Inorg. Chim. Acta, **165**, 73 (1989).
24. A. Kılıç, S. Beğeç, Z. Kılıç, and T. Hokelek. J. Mol. Struct. **516**, 255 (2000).
25. G.A. Carriedo, L.F. Catuxo, F.J.G. Alonso, P.G. Elipe, P.A. Gonzalez, and G. Sanchez. J. Appl. Polym. Sci. **59**, 1879 (1996).
26. H.R. Allcock and M.L. Turner. Macromolecules, **26**, 3 (1993).
27. G.A. Carriedo, L.F. Catuxo, F.J.G. Alonso, P.G. Elipe, and P.A. Gonzalez. Macromolecules, **29**, 5320 (1996).
28. U. Belluco, R. Bertani, R.A. Michelin, M. Mozzan, F. Zingales, and M. Gleria. Inorg. Chim. Acta, **229**, 13 (1995).
29. M.B. McIntosh, T.J. Hartle, and H.R. Allcock. J. Am. Chem. Soc. **121**, 884 (1999).
30. F. Palacios, C. Alonso, G.G. Rubialesa, and J.M. Ezpeleta. Tetrahedron, **60**, 2469 (2004).
31. W. Yuan, L. Zhu, X. Huang, S. Zheng, and X. Tang. Eur. Polym. J. **41**, 1867 (2005).
32. W. Yuan, X. Tang, X. Huang, and S. Zheng. Polymer, **46**, 1701 (2005).
33. G. Fontana, F. Minto, M. Gleria, G. Facchin, R. Bertani, and G. Favero. Eur. Polym. J. **32**, 1273 (1996).
34. T. Muraki, M. Ueta, E. Ihara, and K. Inoue. Polym. Degrad. Stab. **84**, 87 (2004).
35. N. Coşkun and N. Arıkan. Tetrahedron, **55**, 11943 (1999).
36. H.J.P. Lijser, F.H. Fardoun, J.R. Sawyer, and M. Quant. Org. Lett. **4**, 2325 (2002).
37. H.R. Allcock, T.X. Neenan, and W.C. Kossa. Macromolecules, **15**, 693 (1982).
38. G.A. Carriedo, L.F. Catuxo, F.J.G. Alonso, and P.G. Elipe. J. Organomet. Chem. **503**, 59 (1995).