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Synthesis, structural characterization and dielectric behavior of new oxime-cyclotriphosphazene derivatives

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ABSTRACT

The cyclotriphosphazene compound **(2)** bearing formyl groups as side groups was obtained from the reaction of 2,2-Dichloro-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene (**1**) with 4-hydroxy-3-methoxybenzaldehyde in the presence K_2CO_3 in tetrahydrofuran. Oxime-cyclotri phosphazene compound **(3)** was synthesized from the reaction of compound **2** with hydroxylamine hydrochloride in pyridine. The synthesized oxime-phosphazene compound (**3**) was reacted with alkyl and acyl halides. As a results, the cyclotriphosphazene compounds **(1–10)** bearing oxime ether and ester as side groups were obtained. The chemical structures of these compounds **(1–10)** were determined by elemental analysis, FT-IR, ^1H, ^{13}C and ^{31}P NMR spectroscopic methods. Dielectric constant, dielectric loss factors and conductivity properties of cyclotriphosphazene compounds were measured over the frequency range from 100 Hz to 2 kHz at 25 °C and compared with each other. It is found that ester substituted cyclotriphosphazenes have higher dielectric constant. Our study suggests that these phosphazenes promising candidate materials in multifunctional optoelectronic devices.

1. Introduction

Phosphorous-nitrogen double bond containing compounds are called as phosphazene. Generally, linear, cyclic and polyphos phazenes are the three important types. Hexachlorocyclotri phosphazene and poly(dichlorophosphazene) are well known and most studying types of cyclophosphazene and polyphosphazes [1]. Due to the reactivity of chlorine groups in the phosphazene compounds would give various nucleophilic reactions such as aminolysis, alcoholysis, phenolysis and Friedel–Crafts reaction [2–6]. Phosphazene derivatives possess different physical and biological properties such as fluorescence [7,8], flame retardancy [9,10], dielectric and proton conductivity [11–13], catalytic [14], liquid crystals [15], antimicrobial, antibacterial, anti-HIV, anti-leukemic and strong anti-tumor activity [16–22].

Oximes are compounds bearing a carbon nitrogen double bond which are formed by the reaction of aldehyde or ketone with hydroxylamine. Oximes, ($R_1R_2C{=}NOH$), are amphoteric compounds that display basic character because of azomethine (C=N) and exhibit acidic character due to hydroxyl (OH) groups [23]. Oximes have been used in large area of organic, inorganic, analytic, industrial biochemistry for different aims. It is well known that some oxime derivatives have physical and biological activity properties [24–30].

The dielectric constant (permittivity or electrical conductivity) shows how much the energy is stored under the influence of a field in the outer electrical area and how much the energy is lost in the material. Recently, the studies about the dielectric and electric properties of compounds which contain conjugated π electron system were gained importance. The conjugated structures exhibit conductive or semi-conductive properties and these structures display optical and electrical properties such as dielectric constant, refractive index, and impedance. These parameters have great potential in various research areas; from the solar cells and light emitting diode (LED) technologies to nano dimension electronic devices [31–42].

The synthesis and physical properties of cyclophosphazene compounds were reported in the literature [43–51]. But no studies were found about dielectric properties of oxime-cyclophosphazene derivatives.

In this study, oxime cyclophosphazene compound was obtained from 2,2-di[(4-formyl-2-methoxy)phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene, and then oxime-cyclophosphazene was reacted with alkyl and acyl halides in order

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to get new compounds. Dielectric behavior of oxime-cyclotriphosphazene compounds **(2–10)** were investigated due to high polarity of their structure. Dielectric constant, dielectric loss and conductivity parameters of all cyclophosphazene compounds were measured at different frequencies.

2. Experimental

2.1. Materials and methods

Hexachlorocyclotriphosphazene, 2,2′-dioxybiphenol, alkyl and acyl halogens, K_2CO_3, triethylamine and tetrahydrofuran were purchased form Merck and Sigma–Aldrich. Hexachlorocyclotri phosphazene and 2,2′-dioxybiphenol were purified by recrystallization before use. FT-IR spectra of all compounds were recorded with a Perkin Elmer FT-IR instrument using KBr pellets. ^1H, ^{13}C, and ^{31}P NMR spectra of the compounds were recorded using a Bruker DPX-400 spectrometer. Elemental analysis was carried out by a LECO 932 CHNS-O apparatus. For the NMR studies, the chloroform-d and aceton-d_6 were used as solvent for these compounds.

2.2. Synthesis

2,2-Dichloro-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene **(1)** bearing dioxybiphenyl was obtained according to method in the literature [52].

2.2.1. Synthesis of 2,2-di[(4-formyl-2-methoxy)phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene **(2)**

A mixture of **1** (10 g, 17.4 mmol), 4-hydroxy-3-methoxybenzaldehyde (5.30 g, 34.8 mmol) and K_2CO_3 (4.70 g, 34.8 mmol) was stirred in the presence of tetrahydrofuran (200 mL) and then was reacted at room temperature for 24 h. The mixture was filtered. Tetrahydrofuran was removed under vacuum and then extracted with $CHCl_3$ (4 × 25 mL). After the solvent was evaporated, a white solid (**2**) obtained 9.96 g (71%). *Anal.* Calcd. for $C_{40}H_{30}N_3O_{10}P_3$ (805.60): C, 59.64; H, 3.75; N, 5.22. Found: C, 59.74; H, 3.71; N, 5.28%. FT IR (KBr, cm^{-1}): 3071 $\nu_{C\text{-}H(Ar.)}$, 2846 and 2934 $\nu_{C\text{-}H(Aliphatic)}$, 1700 $\nu_{C=O}$, 1476, 1502 and 1597 $\nu_{C=C}$, 1174 and 1230 $\nu_{P=N}$, 931 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.44 (2P, d, $Pa(O_2C_{12}H_8)$), 11.17 (1P, t, $Pb(O_6C_{16}H_{14})$). ^1H NMR (chloroform-d): 3.97 (6H, s, H^{13}), 6.96–7.57 (22H, m, Ar H), 9.97 (s, 2H, H^{14}). ^{13}C NMR (chloroform-d): 147.9 C^1, 121.7 C^2, 129.4 C^3, 122.5 C^4, 134.0 C^5, 128.6 C^6, 145.4 C^7, 152.0 C^8, 110.5 C^9, 129.5 C^{10}, 125.9 C^{11}, 117.5 C^{12}, 56.0 C^{13}, 190.9 C^{14}.

2.2.2. Synthesis of 2,2-di[(4-(hydroxyimino)-2-methoxy)phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene **(3)**

A solution of **2** (10 g, 12.41 mmol) in pyridine (8 mL) was added over a solution of hydroxylamine hydrochloride (1.73 g, 24.82 mmol) and refluxed at 116 °C for 3 h. After the reaction was completed, the mixture was allowed to cool and slowly poured into deionized water (100 mL). After the precipitated solid dried, it was dissolved in acetone and then precipitated from cool water. A white solid (**3**) obtained 9.54 g (92%). *Anal.* Calcd. for $C_{40}H_{32}N_5O_{10}P_3$ (MW = 835.63): C, 57.49; H, 3.86; N, 8.38. Found: C, 57.53; H, 3.79; N, 8.47%. FT-IR (KBr, cm^{-1}): 3340 ν_{OH}, 3060 $\nu_{C\text{-}H(Ar.)}$, 2928 and 2967 $\nu_{C\text{-}H(Aliphatic)}$, 1509, 1586 and 1598 $\nu_{C=C,\ C=N}$, 1174 and 1230 $\nu_{P=N}$, 974 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (acetone-d_6): 25.72 (2P, d, $Pa(O_2C_{12}H_8)$), 11.28 (1P, t, $Pb(O_6C_{16}H_{12}N_2)$). ^1H NMR (acetone-d_6): 3.86 (6H, s, H^{13}), 6.93–7.70 (22H, m, Ar–H), 8.23 (2H, s, H^{14}), 10.52 (2H, s, H^{15}). ^{13}C NMR (acetone-d_6): 147.9 C^1, 121.8 C^2, 129.4 C^3, 121.9 C^4, 134.2 C^5, 128.5 C^6, 141.2 C^7, 151.6 C^8, 110.4 C^9, 129.7 C^{10}, 126.1 C^{11}, 116.9 C^{12}, 55.5 C^{13}, 154.8 C^{14}.

2.2.3. Synthesis of 2,2-di[{(4-(methyloxy)imino)-2-methoxy} phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene **(4)**

To a solution of **3** (0.5 g, 0.60 mmol) and K_2CO_3 (2.4 mmol) in acetone (20 mL) at room temperature was slowly added a solution of methyl chloride (1 mL, 1.2 mmol) in acetone (10 mL) under argon atmosphere. The reaction was heated under reflux for 48 h and cooled to room temperature. The mixture was filtered and precipitated in ice-cold water. The residue was isolated by filtration. The substance was dissolved in chloroform and precipitated with hexane. The mixture was filtered and dried at 24 h in vacuum. A white solid (**4**) formed 0.36 g (70%). *Anal.* Calcd. for $C_{42}H_{36}N_5O_8P_3$ (MW = 863.68): C, 63.08; H, 4.54; N, 8.76. Found: C, 63.16; H, 4.61; N, 8.68%. FT IR (KBr, cm^{-1}): 3071 $\nu_{C\text{-}H(Ar.)}$, 2846 and 2956 $\nu_{C\text{-}H(Aliphatic)}$,1509, 1586 and 1599 $\nu_{C=C,\ C=N}$, 1174 and 1230 $\nu_{P=N}$, 975 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.30 (2P, d, $Pa(O_2C_{12}H_8)$), 11.35 (1P, t, $Pb(O_6C_{16}H_{16}N_2)$). ^1H NMR (chloroform-d): 3.77 (6H, s, H^{13}), 3.95 (6H, s, H^{15}), 6.88–7.53 (22H, m, Ar–H), 8.16 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.8 C^1, 121.6 C^2, 129.3 C^3, 122.3 C^4, 132.8 C^5, 128.5 C^6, 141.8 C^7, 151.6 C^8, 109.4 C^9, 129.5 C^{10}, 125.9 C^{11}, 119.6 C^{12}, 56.2 C^{13}, 156.7 C^{14}, 61.5 C^{15}.

2.2.4. Synthesis of 2,2-di[{(4-(allyloxy)imino)-2-methoxy} phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene **(5)**

To a solution of **3** (0.5 g, 0.60 mmol) and K_2CO_3 (2.4 mmol) in acetone (20 mL) at room temperature was slowly added a solution of allyl bromide (1 mL, 1.2 mmol) in acetone (10 mL) under argon atmosphere. The reaction was heated under reflux for 48 h. And then it cooled to room temperature. The reaction mixture was filtered and poured into ice-cold water (250 mL). The precipitate was isolated by filtration and the substance was dried. The substance was dissolved in chloroform and precipitated with hexane. The solid matter was dried at 24 h in vacuum. A white solid (**5**) formed 0.39 g (71%). *Anal.* Calcd. for $C_{46}H_{40}N_5O_6P_3$ (MW = 915.76): C, 64.86; H, 4.73; N, 8.22. Found: C, 64.92; H, 4.79; N, 8.17%. FT-IR (KBr, cm^{-1}): 3071 $\nu_{C\text{-}H(Ar.)}$, 2934 and 2961 $\nu_{C\text{-}H(Aliphatic)}$, 1509, 1586 and 1599 $\nu_{C=C,\ C=N}$, 1176 and 1230 $\nu_{P=N}$, 975 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.40 (2P, d, $Pa(O_2C_{12}H_8)$), 11.11 (1P, t, $Pb(O_6C_{22}H_{20}N_2)$). ^1H NMR (chloroform-d): 3.03 (4H, d, H^{17}), 3.76 (6H, s, H^{13}), 4.02 (4H, m, H^{16}), 6.83–7.47 (22H, m, Ar–H), 8.16 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.8 C^1, 121.6 C^2, 129.3 C^3, 122.2 C^4, 133.9 C^5, 128.5 C^6, 141.72 C^7, 151.5 C^8, 109.4 C^9, 129.5 C^{10}, 125.9 C^{11}, 120.4 C^{12}, 58.6 C^{13}, 151.5 C^{14}, 66.9 C^{15}, 134.5 C^{16}, 116.6 C^{17}.

2.2.5. Synthesis of 2,2-di[{(4-(benzyloxy)imino)-2-methoxy} phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene **(6)**

To a solution of **3** (0.5 g, 0.60 mmol) and K_2CO_3 (2.4 mmol) in acetone (20 mL) at room temperature was slowly added a solution of benzyl chloride (1 mL, 1.2 mmol) in acetone (10 mL) under argon atmosphere. The reaction was heated under reflux for 12 h, and then cooled to room temperature. The reaction mixture was filtered and poured into ice-cold water (250 mL). The precipitate was isolated by filtration and the solid was dried. The product was dissolved in chloroform and precipitated with hexane. The substance was dried at 24 h in vacuum. A white solid (**6**) formed 0.39 g (65%). *Anal.* Calcd. for $C_{54}H_{44}N_5O_6P_3$ (MW = 1015.88): C, 68.14; H, 4.66; N, 7.36. Found: C, 68.21; H, 4.70; N, 7.41%. FT-IR (KBr, cm^{-1}): 3029 and 3060 $\nu_{C\text{-}H(Ar.)}$, 2868 and 2932 $\nu_{C\text{-}H(Aliphatic)}$, 1508, 1582 and 1598 $\nu_{C=C,\ C=N}$, 1176 and 1230 $\nu_{P=N}$, 973 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.32 (2P, d, $Pa(O_2C_{12}H_8)$), 11.20 (1P, t, $Pb(O_6C_{30}H_{24}N_2)$). ^1H NMR (chloroform-d): 3.75 (6H, s, H^{13}), 4.03 (4H, d, H^{15}), 6.92–7.69 (22H, m, Ar–H), 8.57 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.9 C^1, 121.5 C^2, 129.5 C^3, 121.7 C^4, 134.1 C^5, 129.3 C^6, 141.8 C^7, 151.6 C^8, 109.7 C^9,

129.7 C^{10}, 126.0 C^{11}, 151.4 C^{12}, 56.2 C^{13}, 155.9 C^{14}, 76.0 C^{15}, 128.3 C^{16}, 128.2 C^{17}, 127.7 C^{18}, 128.2 C^{19}.

2.2.6. Synthesis of 2,2-di[{(4-(chloroacetyloxy)imino)-2-methoxy} phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene ***(7)***

To a solution of **3** (0.5 g, 0.60 mmol) and triethyl amine (0.17 mL, 2.4 mmol) in tetrahydrofuran (20 mL) at room temperature was slowly added a solution of chlorine acetyl chloride (1 mL, 1.2 mmol) in tetrahydrofuran (10 mL) under argon atmosphere. The reaction was stirred at room temperature for 24 h. The reaction mixture was filtered and poured into water (250 mL). The precipitate was isolated by filtration. The product was dissolved in chloroform and precipitated with hexane. The product was dried at 24 h in vacuum. A white solid (**7**) formed 0.44 g (75%). *Anal.* Calcd. For $C_{44}H_{34}Cl_2N_5O_8P_3$ (MW = 988.60): C, 57.16; H, 3.71; N, 7.57. Found: C, 57.23; H, 3.80; N, 7.49%. FT-IR (KBr, cm^{-1}): 3071 $\nu_{C\text{-}H(Ar.)}$, 2851, 2927 and 2950 $\nu_{C\text{-}H(Aliphatic)}$, 1782 $\nu_{C=O,}$ 1508, 1586 and 1599 $\nu_{C=C,\ C=N}$, 1174 and 1230 $\nu_{P=N}$, 974 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.22 (2P, d, $Pa(O_2C_{12}H_8)$), 10.88 (1P, t, $Pb(O_6C_{22}H_{14}N_2Cl_2)$). ^1H NMR (chloroform-d): 3.98 (6H, s, H^{13}), 4.36 (4H, d, H^{16}), 7.02–7.62 (22H, m, Ar–H), 8.43 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.8 C^1, 121.6 C^2, 129.5 C^3, 122.4 C^4, 133.7 C^5, 128.6 C^6, 149.1 C^7, 151.8 C^8, 110.2 C^9, 126.9 C^{10}, 125.9 C^{11}, 115.4 C^{12}, 56.2 C^{13}, 156.5 C^{14}, 170.3 C^{15}, 40.5 C^{16}.

2.2.7. Synthesis of 2,2-di[{(4-(propanoyloxy)imino)-2-methoxy} phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene ***(8)***

To a solution of **3** (0.5 g, 0.60 mmol) and triethyl amine (0.17 mL, 2.4 mmol) in tetrahydrofuran (20 mL) at room temperature was slowly added a solution of propanoyl chloride (1 mL, 1.2 mmol) in tetrahydrofuran (10 mL) under argon atmosphere. The reaction was stirred at room temperature for 24 h. The reaction mixture was filtered and poured into water (250 mL). The precipitate was isolated by filtration. The product was dissolved in chloroform and precipitated with hexane. The substance was dried at 24 h in vacuum. A white solid (**8**) formed 0.42 g (75%). *Anal.* Calcd. For $C_{46}H_{40}N_5O_{12}P_3$ (MW = 947.76): C, 58.29; H, 4.25; N, 7.39. Found: C, 58.36; H, 4.30; N, 7.44%. FT-IR (KBr, cm^{-1}): 3060 $\nu_{C\text{-}H(Ar.)}$, 2978 $\nu_{C\text{-}H(Aliphatic)}$, 1765 $\nu_{C=O,}$ 1508, 1583 and 1598 $\nu_{C=C,\ C=N}$, 1174 and 1230 $\nu_{P=N}$, 974 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.20 (2P, d, $Pa(O_2C_{12}H_8)$), 10.93 (1P, t, $Pb(O_8C_{22}H_{20}N_2)$). ^1H NMR (chloroform-d): 1.33 (6H, t, H^{17}), 2.44 (4H, q, H^{16}), 3.95 (6H, s, H^{13}), 7.01–7.56 (22H, m, Ar–H), 8.36 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.8 C^1, 121.4 C^2, 128.6 C^3, 121.6 C^4, 129.5 C^5, 127.8 C^6, 143.1 C^7, 151.7 C^8, 110.2 C^9, 129.4 C^{10}, 125.9 C^{11}, 115.4 C^{12}, 55.8 C^{13}, 155.2 C^{14}, 171.9 C^{15}, 26.3 C^{16}, 8.9 C^{17}.

2.2.8. Synthesis of 2,2-di[{(4-(o-chlorobenzoyloxy)imino)-2-methoxy}phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene ***(9)***

To a solution of **3** (0.5 g, 0.60 mmol) and triethyl amine (0.17 mL, 2.4 mmol) in tetrahydrofuran (20 mL) at room temperature was slowly added a solution of *o*-chlorobenzoyl chloride (1 mL, 1.2 mmol) in tetrahydrofuran (10 mL) under argon atmosphere. The reaction was stirred at room temperature for 24 h. The reaction mixture was filtered and poured into water (250 mL). The precipitate was isolated by filtration. The substance was dissolved in chloroform and was precipitated with hexane. The product was dried at 24 h in vacuum. A white solid (**9**) formed 0.48 g (72%). *Anal.* Calcd. For $C_{54}H_{38}Cl_2N_5O_8P_3$ (MW = 1112.73): C, 61.84; H, 3.65; N, 6.68. Found: C, 61.89; H, 3.70; N, 6.73%. FT IR (KBr, cm^{-1}): 3068 $\nu_{C\text{-}H(Ar.)}$, 2937 and 2972 $\nu_{C\text{-}H(Aliphatic)}$, 1758 $\nu_{C=O,}$ 1475, 1507 and 1590 $\nu_{C=C,\ C=N}$, 1174 and 1233 $\nu_{P=N}$, 974 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.29 (2P, d, $Pa(O_2C_{12}H_8)$), 10.91 (1P, t, $Pb(O_8C_{30}H_{18}N_2Cl_2)$). ^1H NMR (chloroform-d): 3.97 (6H, s, H^{13}), 6.99–7.90 (30H, m, Ar H), 8.49 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.9 C^1, 121.6 C^2, 129.4 C^3, 122.3 C^4, 134.1 C^5, 128.6 C^6, 147.9 C^7, 151.8 C^8, 110.2 C^9, 126.4 C^{10}, 125.9 C^{11}, 115.4 C^{12}, 56.1 C^{13}, 156.5 C^{14}, 163.5 C^{15}, 129.5 C^{16}, 141.8 C^{17}, 131.7 C^{18}, 136.9 C^{19}, 127.5 C^{20}, 133.1 C^{21}.

2.2.9. Synthesis of 2,2-di[{(4-(thiophene-2-carbonyloxy)imino)-2-methoxy}phenoxy]-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene ***(10)***

To a solution of **3** (0.5 g, 0.60 mmol) and triethyl amine (0.17 mL, 2.4 mmol) in tetrahydrofuran (20 mL) at room temperature was slowly added a solution of thiophene-2-carbonyl chloride (1 mL, 1.2 mmol) in tetrahydrofuran (10 mL) under argon atmosphere. The reaction was stirred at room temperature for 24 h. The reaction mixture was filtered. The mixture was precipitated in water. The residue was isolated by filtration. The product was dissolved in chloroform and was precipitated with hexane. The substance was dried at 24 h in vacuum. A white solid (**10**) formed 0.43 g (68). *Anal.* Calcd. For $C_{50}H_{36}N_5O_8P_3$ (MW = 1055.90): C, 60.54; H, 3.66; N, 7.06. Found: C, 60.60; H, 3.72; N, 7.13%. FT-IR (KBr, cm^{-1}): 3087 $\nu_{C\text{-}H(Ar.)}$, 2935 and 2972 $\nu_{C\text{-}H(Aliphatic)}$, 1738 $\nu_{C=O,}$ 1509, 1583 and 1597 $\nu_{C=C,\ C=N}$, 1171 and 1230 $\nu_{P=N}$, 973 $\nu_{P\text{-}O\text{-}C}$. ^{31}P NMR (chloroform-d): 25.37 (2P, d, $Pa(O_2C_{12}H_8)$), 11.23 (1P, t, $Pb(O_8C_{26}H_{16}N_2S_2)$). ^1H NMR (chloroform-d): 3.94 (6H, s, H^{13}), 6.98–7.93 (28H, m, Ar H), 8.50 (2H, s, H^{14}). ^{13}C NMR (chloroform-d): 147.9 C^1, 121.6 C^2, 129.9 C^3, 122.9 C^4, 134.1 C^5, 128.6 C^6, 143.3 C^7, 151.8 C^8, 110.2 C^9, 126.4 C^{10}, 125.9 C^{11}, 116.2 C^{12}, 55.8 C^{13}, 155.9 C^{14}, 163.5 C^{15}, 135.2 C^{16}, 128.3 C^{17}, 124.0 C^{18}, 133.1 C^{19}.

2.3. Dielectric and electrical properties

The dielectric properties of oxime ester and ether bearing cyclotriphosphazene **(4–10)** were examined. All compounds **(2–10)** were formed into a pellet under 4 Mpa pressure. These pellets were placed between electrodes of impedance analyzer device. And then the capacitance values (Cp) of cyclotriphosphazene compounds **(2–10)** were measured a functional the frequency range from 100 Hz to 4 kHz at 25 °C. The dielectric constant and dielectric loss factors were calculated below Equations (1) and (2).

$$\varepsilon' = \boldsymbol{C_p}\frac{\boldsymbol{d}}{\boldsymbol{A}\varepsilon_0} \tag{1}$$

$$\varepsilon'' = \varepsilon' \mathrm{DF} \tag{2}$$

Where ε' is dielectric constant, ε_0 is the dielectric constant of vacuum (8.854×10^{-12}), d is the thickness (m) and A is effective area (m^2) of the sample and C is the capacitance (F) of test device. Dielectric properties of the cyclotriphosphazene compounds **(2–10)** were studied with QuadTech 7600 Impedance/Gain Analyzer.

The conductivity values (Gp) of oxime-ether and ester containing cyclotriphosphazene compounds **(4–10)** were measured over the frequency range from 100 Hz to 4 kHz by impedance analyzer. And then the electrical conductivity values (AC conductivity) were calculated below Equation (3).

$$\boldsymbol{\sigma} = \boldsymbol{G_p}\frac{\boldsymbol{d}}{\boldsymbol{A}} \tag{3}$$

Where σ is ac conductivity, d is the thickness (m) and A is effective area (m^2) of the sample.

3. Results and discussion

3.1. Synthesis and characterization

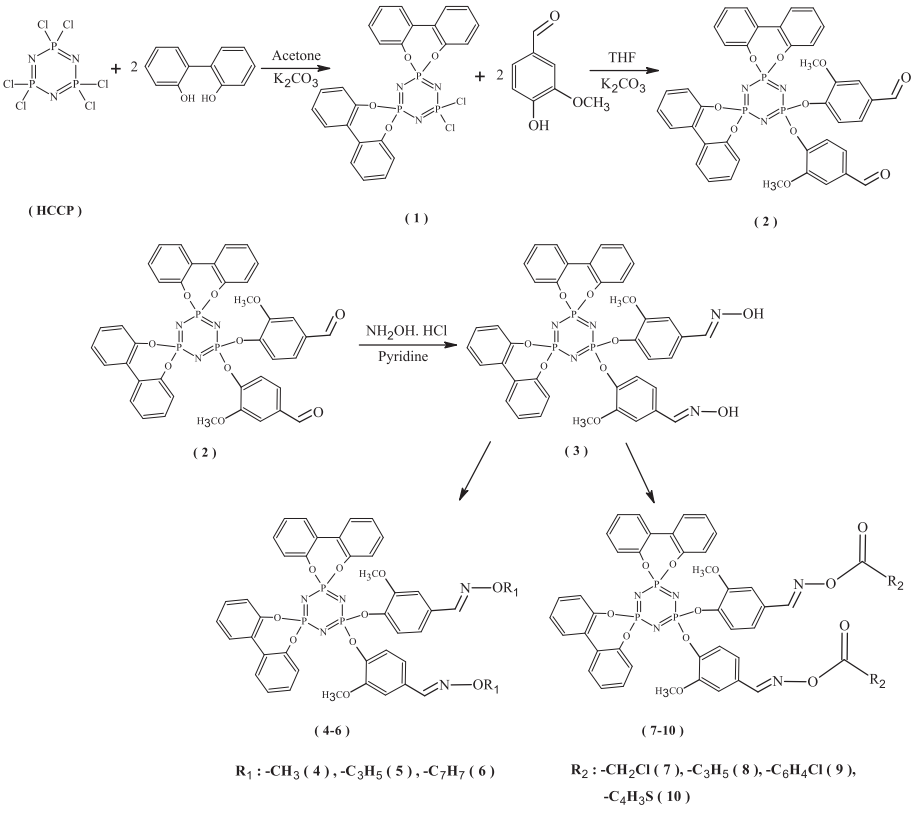
2,2-Bis(4-formyl-2-methoxyphenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)] cyclotriphosphazene **(2)** was obtained from the reaction of **1** with 2 equiv. of 4-hydroxy-3-methoxybenzaldehyde in the presence of K_2CO_3 in tetrahydrofuran (THF). New Oxime-phosphazene 2,2-Bis(4-[hydroxyimino]-2-methoxyphenoxy)-4,4,6,6-bis[spiro(2′,2″-dioxy-1′,1″-biphenylyl)]cyclotriphosphazene **(3)** was obtained by the interaction of **2** with hydroxylamine hydrochloride in pyridine. Disubstituted compounds were synthesized by reacting compound **3** with benzyl chloride, allyl bromide, propanoyl chloride, 2-chlorobenzoyl chloride, chloroacetyl chloride, methyl iodide and thiophene-2-carbonyl chloride in the presence of triethyl amine/K_2CO_3 in THF/acetone. Oxime-phosphazene compounds were characterized by ^1H, ^{13}C and ^{31}P NMR, elemental analysis and FT-IR spectroscopy. General representation of the reactions and structures are shown in Scheme 1 and Scheme 2.

The characteristic signals in the ^{31}P, ^1H, ^{13}C NMR and FT-IR spectra of the cyclotriphosphazene compounds **(2–10)** have been appointed in the Experimental section. In the FT-IR spectra of compounds **1–10,** the -P=N stretching vibrations were observed between 1171 and 1179 cm^{-1}. The aldehyde carbonyl stretching vibration was observed at 1700 cm^{-1} for compound **2**. The presence of –OH stretching vibration and the absence of aldehyde carbonyl bands in the compound **3** indicate the oxime compound. The absence of the OH stretching vibration in the FT-IR spectra of **4–10** indicates that all hydrogen atoms of the OH groups have been replaced. The P–O–C stretching vibrations in the compounds **1–10** were observed between 935 and 937 cm^{-1}. The ester carbonyl band was observed between 1738 and 1782 cm^{-1} for **7–10**. The FT-IR spectrum of **3** is depicted in Fig. 5.

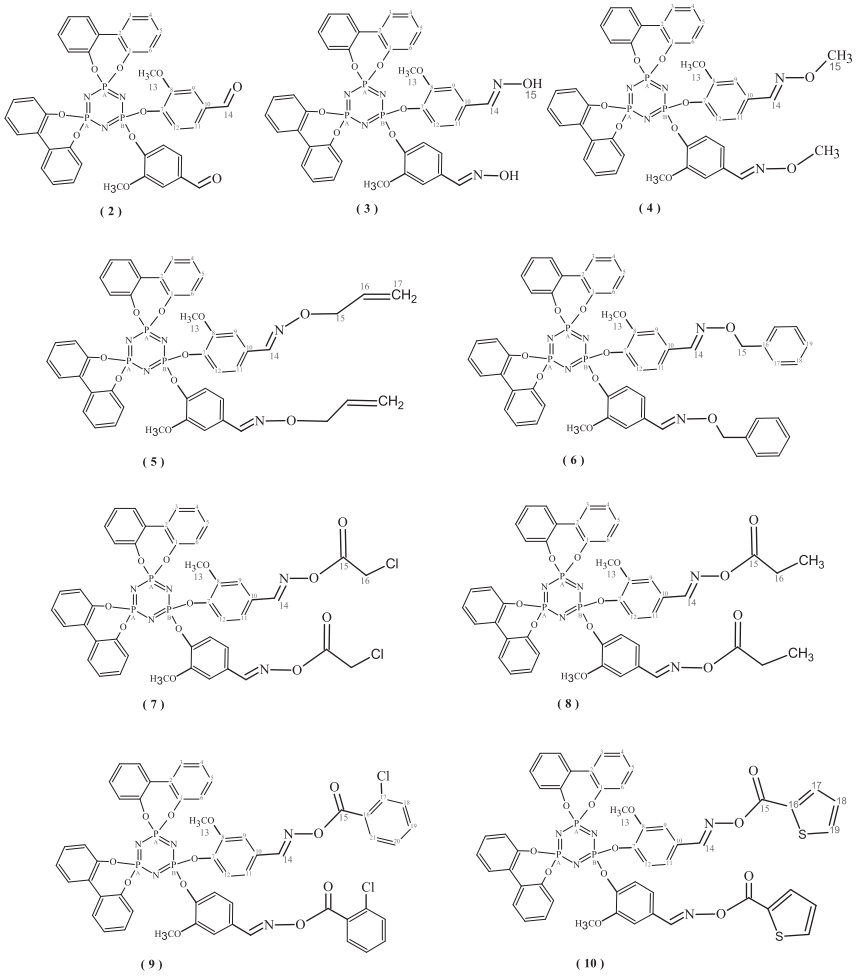
The ^{31}P NMR data for **1–10** are represented in experimental section (AB_2 system). There are two peaks in the ^{31}P NMR spectra of substituted cyclotriphosphazene compounds **(1–10)**. The ^{31}P NMR spectra of compound **1** was showed at $\delta = 19.90$ and 29.60 ppm in a triplet-doublet. In the ^{31}P NMR spectra for compound **2** was observed at $\delta = 11.17$ and 25.44 ppm in a triplet-doublet. The ^{31}P NMR spectra of oxime-phosphazene and derivatives not observed significant a change, because of oxime ether and ester groups make almost no change the electron density on the phosphorus atoms. The ^{31}P NMR spectrum of **3** is depicted in Fig. 1.

The structures of compounds **1–10** were identified by ^1H NMR and ^{13}C NMR methods (Scheme 2). In the ^1H NMR spectra of **4–10**, the absence of the OH protons indicates substituted phosphazene products. The methyl protons for **4** and **8** were observed at 3.95 and 1.33 ppm, respectively. The methylene protons for **5** were observed at 3.03 and 4.02 ppm, respectively. The methylene protons for **6, 7** and **8** were observed at 4.03, 4.36 and 2.44 ppm, respectively. The aromatic protons for **2–10** were showed between 6.88 and 7.93 ppm. The azomethine protons for compounds **3–10** were showed at between 8.16 and 8.57 ppm. The aldehyde carbonyl protons were not observed in ^1H NMR spectrum of compound **3**. The –OH peaks of the oxime were not observed in ^1H NMR spectrum of compounds **4–10**.

The aldehyde carbonyl carbons in the ^{13}C NMR spectrum of **2** were observed at 190.98 ppm. The aldehyde carbonyl carbons were not showed in the ^{13}C NMR spectrum of compound **3**. The azomethine carbons of compounds **3–10** were showed at between 151.54 and 156.65 ppm. The ester carbonyl carbon atoms (C=O) in the compounds **7, 8, 9 and 10** were observed at 170.30, 171.88, 189.29, 163.45 and 163.54 ppm, respectively. The methyl carbons



Scheme 1. General presentation of cyclotriphosphazene derivatives.



Scheme 2. The structures of compounds **2**–**10**.

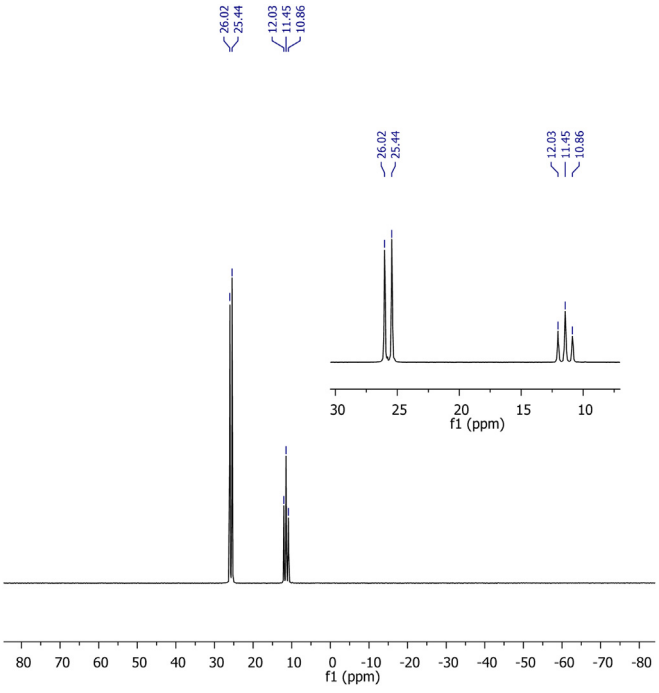


Fig. 1. ^{31}P NMR spectrum of compound **3** (acetone-d_6).

for **4** and **8** were observed at 61.52 and 8.85 ppm, respectively. The methylene carbons for compounds **6, 7** and **8** were observed at 76.02, 40.53 and 26.26 ppm, respectively.

3.2. Dielectric behavior

The dielectric and electrical properties of cyclotriphosphazene compounds bearing oxime ester and ether groups were investigated towards the frequency range from 100 Hz to 4 kHz. In this manner, the dielectric constant, dielectric loss and conductivity of cyclotriphosphazene derivatives **(2**–**10)** were measured by impedance analyzer device. The measured dielectric constant of oxime-eter compounds (**4**, **5** and **6**) and oxime-ester compounds (**7**, **8** and **9**) containing cyclotriphosphazene compounds were compared in Fig. 2. According to the obtained results, the dielectric constants have been reduced against increasing frequency. Especially, decreases in the dielectric constants have been obvious at low frequency values (1–1000 Hz). On the other hand, when closing the higher frequency levels, decline of the dielectric constants get reduced. The reason behind acquired results is that existence of polar groups on the structure which leads to increase dielectric constant [11,41]. The carbonyl group which is bonded to oxime-ester groups made dielectric constant higher compare to other derivatives.

The changes in the dielectric loss factors were showed similar behavior with dielectric constant. In Fig. 3, dielectric loss factors of

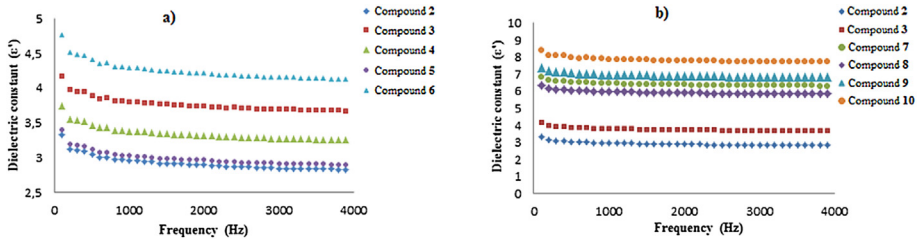


Fig. 2. Variation of dielectric constant of cyclotriphosphazene compounds **(2–10)**; a) oxime-ether compounds **(4–6)**, b) oxime-ester compounds **(7–10)**.

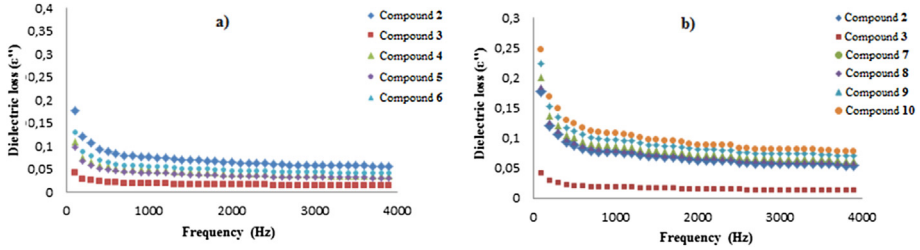


Fig. 3. Variation of dielectric loss of cyclotriphosphazene compounds **(2–10)**; a) oxime-ether compounds **(4–6)**, b) oxime-ester compounds **(7–10)**.

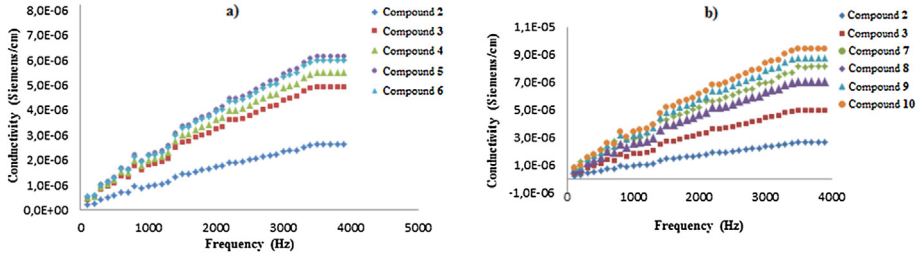


Fig. 4. Variation of AC conductivity of cyclotriphosphazene compounds **(2–10)**; a) oxime-ether compounds **(4–6)**, b) oxime-ester compounds **(7–10)**.

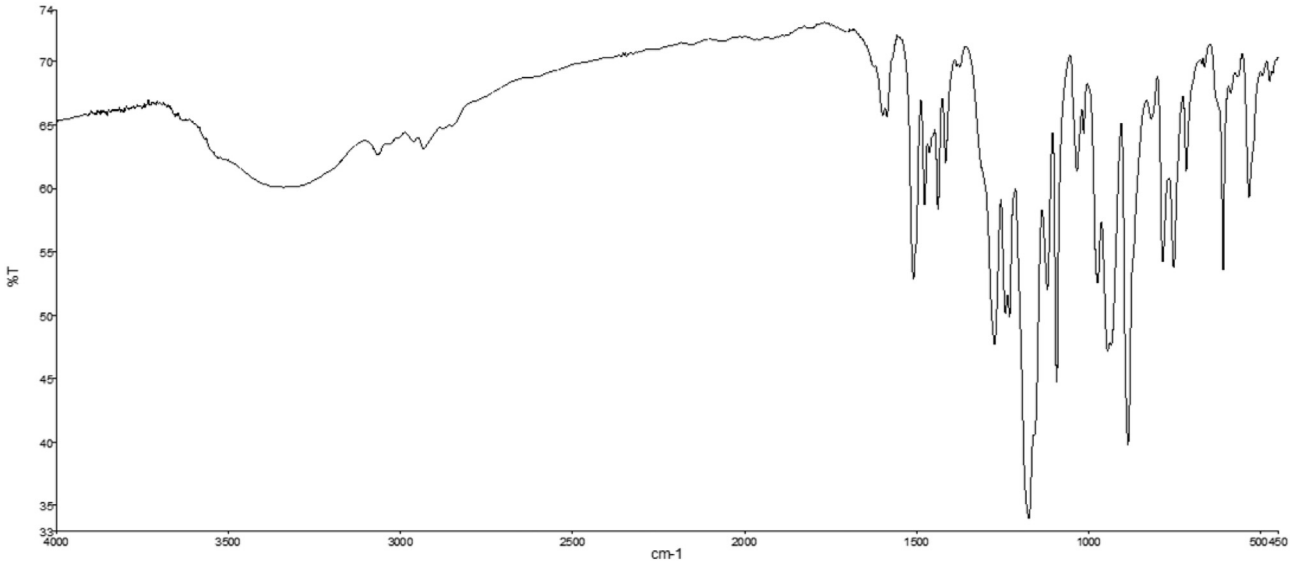


Fig. 5. FT-IR spectrum of compound **3**.

oxime-ether and ester containing cyclotriphosphazene compounds **(4–10)** were reduced against increasing frequencies values. Decreasing of the dielectric loss factors proved that the existence of surface polarization in these compounds **(4–10)** at increased frequencies. The similar studies were reported in the literature [53].

The conductivity results of oxime and ether containing phosphazene derivatives **(4–10)** were given at Fig. 4. Electrical conductivity of cyclotriphosphazene compounds **(2–10)** were

Table 1
The dielectric constant (ε′) and AC conductivity (σ) values of cyclotriphosphazene compounds **(2–10)** in the frequency of 1 kHz and at 25 °C.

Compounds	ε′	σ (Siemens/cm)
2	2,95	$9,5 \times 10^{-7}$
3	3,80	$1,79 \times 10^{-6}$
4	3,37	$1,99 \times 10^{-6}$
5	3,02	$2,17 \times 10^{-6}$
6	3,80	$2,24 \times 10^{-6}$
7	6,44	$2,88 \times 10^{-6}$
8	5,96	$2,57 \times 10^{-6}$
9	6,95	$3,19 \times 10^{-6}$
10	7,87	$3,41 \times 10^{-6}$

increased with raising frequencies. The rapid rise of AC (alternating-current) conductivity in the low frequencies is remained constant at the higher frequencies.

The oxime-ester phosphazene compound **10** containing thiophene group displayed higher conductivity than other cyclotriphosphazene compounds. For example, the dielectric constant (**ε′**) and AC conductivity (**σ**) values for compound **4** was observed at 3.37 and 1.99×10^{-6}, respectively. But these ε′ and σ values for compound **10** were observed at 7.87 and 3.41×10^{-6}, respectively. It is believed that this increase came from the presence of polar groups and π electron conjugation in the structure of compound **10** such as carbonyl (C═O) and thiophene [11,37]. The dielectric constant and conductivity values of cyclotriphosphazene compounds **(2–10)** in the frequency of 1 kHz and at room temperature are given in Table 1.

4. Conclusion

The cyclotriphosphazene compounds containing oxime ether and ester as side groups **(4–10)** were obtained from the interaction of alkyl or acyl halides with oxime-cyclotriphosphazene **3**. The dielectric and electrical properties of cyclotriphosphazene compounds **(2–10)** were investigated against frequencies (100 Hz–4 kHz) at room temperature and compared with each other. The changes in the dielectric constants and dielectric loss factors were showed similar behavior with dielectric constant. Generally, dielectric constant and dielectric loss values were reduced with increasing frequencies. AC conductivity values were raised with increasing frequencies. Oxime-cyclotriphosphazene compounds containing ester as side groups **(7, 8, 9** and **10)** have shown that the higher conductivity values than other cyclotriphosphazenes.

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