

Synthesis, characterization and dielectric properties of phosphazenes containing chalcones



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ABSTRACT

The new hexasubstitue-cyclophosphazene compounds containing chalcone derivatives (**2–11**) were obtained from the reactions of hexachlorocyclotriphosphazene (**1**) with several hydroxy chalcones in K₂CO₃/acetone system. All products were generally obtained in high yields. The structures of the compounds were defined by elemental analysis, FT-IR, ¹H, ¹³C and ³¹P NMR spectroscopy. Dielectric measurements for phosphazenes containing chalcone compounds (**5–8**) were carried out by means of an impedance analyzer as a function of temperature and frequency. Dielectric properties of samples prepared in a plate form were measured at room temperature over the frequency range 50 Hz to 2 kHz and given as compared with each other.

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1. Introduction

Phosphazenes are compounds containing a phosphorus–nitrogen double bond in their skeleton. They are also known as imino-phosphoranes and phosphine imides. Phosphazenes fall into three categories: the cyclo-, poly-, and monophosphazenes. The cyclo- and polyphosphazenes probably are the best known and most intensively studied phosphorus–nitrogen compounds because they are more stable than monophosphazenes [1]. The properties of phosphazene materials can be varied over a broad range by attaching different substituents to the main backbone [2]. The synthesis of phosphazene compounds has become significant, because phosphazene compounds have many potential applications, including biomaterials [3], drug delivery systems [4,5], fuel cell membranes [6,7], ionic conductors [8], flame retardants [9] and optical materials [10,11]. The study of gas permeability and separations of phosphazene derivatives membrane such as (NPR₂)_n or (NPR¹R²)_n has received special attention in industrial and academic research [11]. For example, polyphosphazenes containing suitable side groups can be used as membrane separators in the field of gas permeation [12], organic liquid separation and evaporation [13–16], ion separation [17], ultra filtration [18] and micro filtration [19]. Cyclophosphazenes such as N₃P₃Az₆, N₄P₄Az₈ and N₄P₄pyr₈ were

reported to have the function of anticancer agents [20–24]. It has been demonstrated that some phosphazenes were suitable for development of implantable antitumor devices [11,25].

Chalcones are an important class of natural compounds. They are precursors in flavonoid biosynthesis and they also play an ecological role in relation to plant color [26,27]. Synthetic chalcones and their heterocyclic analogues are most commonly prepared by means of various modifications of the Claisen–Schmidt condensation [28,29]. Another general route involves the Friedel–Crafts acylation of a substituted aromatic compound with a substituted cinnamoyl chloride derivative [30]. Due to the presence of the reactive ketovinyl group in their molecules chalcones and their analogues exhibit various biological activities, such as antibacterial [31–33], antiviral [34], antiprotozoal [35], antifungal [36,37], anti-inflammatory [30,38], and antineoplastic [39]. The mode of antibacterial action has been suggested to be by the reaction of chalcones with important thiol groups on essential enzymes [31,40].

Dielectric constant measurements are one of the most popular methods of evaluating solid materials such as electric insulators and polymers, because dielectric constant measurements can be performed easier than chemical analysis techniques. Impedance spectroscopy is a relatively new and powerful method of characterizing many of the electrical properties of electrolyte materials and their interfaces with electronically conducting electrodes. Permittivity of a material describes its ability to absorb, transmit and

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reflect electromagnetic energy. Permittivity is a complex quantity, consisting of the dielectric constant (ϵ') and the dielectric loss factor (ϵ''), where ϵ' is the real component and is related to the capacitance of the substance and its ability to store electrical energy and ϵ'' is the imaginary component and is related to various absorption mechanisms of energy dissipation [41–43].

The literature contains reports on the synthesis of different linear, cyclic or poly phosphazenes [44–57]. There are limited reports (only three reports) in literature on the synthesis of phosphazenes containing chalcone derivatives [58–60].

In view of the important properties of the chalcone derivatives and phosphazene compounds, it was planned to the synthesis of some new phosphazene derivatives bearing different chalcones, such derivatives could possess interesting and useful properties. In this study, 4'-hydroxy chalcones were prepared by reaction of 4-hydroxyacetophenone with different benzaldehydes according to a method reported in the literature [28,29]. New cyclophosphazenes containing chalcones were hereby isolated for the first time from the reactions of (**1**) with 4'-hydroxy chalcones in acetone in the presence of K_2CO_3 . Dielectric properties of the compounds **5–8** were also investigated in this study. The dielectric constant and dielectric loss behavior of the investigated samples were studied as a function of frequency. The conductance (Gp) parameter, was measured as a function of frequency in the range from 50 Hz to 2 kHz, in the room temperature (25 °C).

2. Experimental

2.1. Materials

Solvents and other liquids were dried by conventional methods. Hexachlorocyclotriphosphazene was recrystallized from hexane. Other chemicals were used as purchased. 4'-hydroxy chalcones were prepared by reaction of 4-hydroxyacetophenone with different benzaldehydes according to a method reported in the literature [28,29]. The reactions of (**1**) with hydroxy chalcones were carried out under dry nitrogen. The deuterated solvents (Chloroform-d and DMSO-d₆) for NMR spectroscopy and the following chemicals were obtained from Merck; acetone, ethanol, K_2CO_3 , anhydrous $MgSO_4$, NaOH, KOH, CH_2Cl_2 and silica gel 60.

2.2. Equipment

FT-IR spectra were recorded on an Perkin Elmer FT-IR spectrometer. Microanalysis was carried out by a LECO 932 CHNS-O apparatus. 1H , ^{13}C , and ^{31}P NMR spectra were recorded using a Bruker DPX-400 spectrometer. The 1H , ^{13}C and ^{31}P NMR chemical shifts were measured using tetramethylsilane as an internal standard, whereas those for ^{31}P were measured using 85% H_3PO_4 as an external standard. For the NMR studies, the DMSO-d₆ was used as solvent for the compounds **3**, **6**, **7** and **11**. The chloroform-d was used as solvent for the compounds **2**, **4**, **5**, **8**, **9** and **10**. Chemical shifts down field from the standard were assigned positive δ values. In the results of NMR spectra, s, d, t and m indicate singlet, doublet, triplet and multiplet respectively. Dielectric properties were carried out at room temperature with a QuadTech 7600 precision LRC Meter impedance analyzer over the frequency range 50 Hz to 2 kHz.

2.3. Synthesis

2.3.1. General synthetic procedures for 4'-hydroxy chalcones

4'-Hydroxy chalcones were prepared according to a method reported in the literature [28,29]. The general method for the synthesis of 4'-hydroxy chalcones is stated as below:

To a solution of 4'-hydroxyacetophenone in ethanol (10 mL/mmol) was added the appropriate substituted aldehyde (1.5 equiv). The mixture was stirred for 15 min, followed by addition of an aqueous solution KOH (3 equiv) at 0 °C. The mixture was refluxed overnight. After the reaction reached completion, it was quenched with water (20 mL). The resulting mixture was concentrated in vacuo, diluted with water (50 mL), acidified with 1 M HCl to pH 3, and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residual solid was purified by column chromatography to yield the desired product.

2.3.2. Synthesis of compound (**2**)

A mixture of hexachlorotriphosphazene (**1**) (1.0 g, 2.88 mmol), 4'-hydroxychalcone (**a**) (5.16 g, 23.01 mmol) and K_2CO_3 (3.18 g, 23.01 mmol) was stirred in acetone (100 mL) at 0 °C and then was reacted at ambient temperature for 24 h. The solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 (4×25 mL). The solvent was concentrated on a rotary evaporator under reduced pressure. The residue was dissolved in chloroform and washed with 10% NaOH solution for three times and then with water, dried over anhydrous magnesium sulfate. The solvent was concentrated on a rotary evaporator under reduced pressure. After the solvent was removed, a white solid (**2**) formed 3.48 g (82%). *Anal. Calc.* for $[C_{90}H_{66}N_3O_{12}P_3]$ (MW = 1474.42): found: C, 73.01; H, 4.59; N, 2.88%; requires: C, 73.31; H, 4.51; N, 2.85%. FT-IR (KBr, cm^{-1}): 3059 and 3001 ν_{Ar-CH} , 2923 $\nu_{Aliphatic-CH}$, 1657 $\nu_{C=O}$, 1598, 1574 and 1500 $\nu_{C=C}$, 1183 and 1207 $\nu_{P=N}$, 1287 ν_{P-N-P} , 949 ν_{P-O-C} . ^{31}P NMR ($CDCl_3$) δ/ppm : 8.27 (s). 1H NMR ($CDCl_3$) δ/ppm : 7.93 (12H, d, H^3), 7.73 (6H, d, H^7), 7.60 (12H, t, H^{10}), 7.51 (6H, d, H^6), 7.41–7.43 (18H, m, H^9 and H^{11}), 7.12 (12H, d, H^2), ^{13}C NMR ($CDCl_3$) δ/ppm : 188.59 C^5 , 153.27 C^1 , 145.24 C^7 , 135.41 C^8 , 134.46 C^4 , 130.52 C^3 , 130.18 C^{10} , 128.72 C^9 , 128.56 C^{11} , 120.89 C^6 , 120.81 C^2 .

The same general procedure gave compounds (**3–11**), with scale (gram, mmol [**b-m**]), reaction times, yield, and spectroscopy data given below.

2.3.3. Synthesis of compound (**3**)

4'-Hydroxy-4-methoxychalcone (**b**) (5.85 g, 23.01 mmol), 24 h. Yield: 3.81 g, 80%. *Anal. Calc.* for $[C_{96}H_{78}N_3O_{18}P_3]$ (MW = 1654.57): found: C, 69.72; H, 4.71; N, 2.49%; requires: C, 69.69; H, 4.75; N, 2.54%. FT-IR (KBr, cm^{-1}): 3065 and 3000 ν_{Ar-CH} , 2932 $\nu_{Aliphatic-CH}$, 1660 $\nu_{C=O}$, 1597, 1571 and 1511 $\nu_{C=C}$, 1178 and 1202 $\nu_{P=N}$, 1293 ν_{P-N-P} , 947 ν_{P-O-C} . ^{31}P NMR (DMSO-d₆) δ/ppm : 8.39 (s). 1H NMR (DMSO-d₆) δ/ppm : 7.88 (12H, d, H^3), 7.67 (6H, d, H^7), 7.52 (6H, d, H^6), 7.35 (12H, d, H^9), 7.07 (12H, d, H^2), 6.90 (12H, d, H^{10}), 3.84 (18H, s, H^{14}), ^{13}C NMR (DMSO-d₆) δ/ppm : 188.61 C^5 , 161.58 C^{11} , 152.84 C^1 , 145.07 C^7 , 135.64 C^4 , 130.41 C^3 , 130.09 C^8 , 127.24 C^9 , 120.86 C^2 , 118.45 C^6 , 114.13 C^{10} , 055.26 C^{14} .

2.3.4. Synthesis of compound (**4**)

4'-Hydroxy-2-methoxychalcone (**c**) (5.85 g, 23.01 mmol), 24 h. Yield: 3.33 g, 70%. *Anal. Calc.* for $[C_{96}H_{78}N_3O_{18}P_3]$ (MW = 1654.57): found: C, 69.67; H, 4.77; N, 2.51%; requires: C, 69.69; H, 4.75; N, 2.54%. FT-IR (KBr, cm^{-1}): 3071 and 3000 ν_{Ar-CH} , 2936 $\nu_{Aliphatic-CH}$, 1660 $\nu_{C=O}$, 1598, 1572 and 1501 $\nu_{C=C}$, 1181 and 1203 $\nu_{P=N}$, 1287 ν_{P-N-P} , 947 ν_{P-O-C} . ^{31}P NMR ($CDCl_3$) δ/ppm : 7.94 (s). 1H NMR ($CDCl_3$) δ/ppm : 8.08 (6H, d, H^7), 7.96 (12H, d, H^3), 7.67 (6H, d, H^{13}), 7.60 (6H, d, H^6), 7.37 (6H, t, H^{11}), 7.14 (12H, d, H^2), 6.99 (6H, t, H^{12}), 6.91 (6H, d, H^{10}), 3.87 (18H, s, H^{14}), ^{13}C NMR ($CDCl_3$) δ/ppm : 188.66 C^5 , 169.39 C^9 , 151.33 C^1 , 145.44 C^7 , 135.66 C^4 , 129.38 C^3 , 129.35 C^{12} , 129.14 C^6 , 128.01 C^{11} , 126.14 C^{13} , 119.99 C^2 , 118.23 C^6 , 116.39 C^{10} , 050.46 C^{14} .

2.3.5. Synthesis of compound (5)

4'-Hydroxy-2-fluorochoalcone (**d**) (5.57 g, 23.01 mmol), 24 h. Yield: 3.41 g, 75%. *Anal. Calc.* for $[C_{90}H_{60}F_6N_3O_{12}P_3]$ (MW = 1582.36): found: C, 68.23; H, 3.85; N, 2.69%; requires; C, 68.31; H, 3.82; N, 2.66%. FT-IR (KBr, cm^{-1}): 3063 and 3001 ν_{Ar-CH} , 2956 $\nu_{Aliphatic-CH}$, 1665 $\nu_{C=O}$, 1605, 1576 and 1502 $\nu_{C=C}$, 1184 and 1207 $\nu_{P=N}$, 1282 ν_{P-N-P} , 952 ν_{P-O-C} . ^{31}P NMR($CDCl_3$) δ/ppm : 7.97 (s). 1H NMR ($CDCl_3$) δ/ppm : 7.98 (12H, d, H^3), 7.74 (6H, d, H^7) 7.68 (6H, t, H^{11}), 7.58 (6H, d, H^{13}), 7.48 (6H, d, H^6), 7.14–7.19 (18H, m, H^2 and H^{12}), 7.107 (6H, d, H^{10}), ^{13}C NMR ($CDCl_3$) δ/ppm : 188.65 C^5 , 163.03 C^9 , 153.62 C^1 , 137.83 C^7 , 135.36 C^4 , 132.05 C^3 , 130.44 C^8 , 129.70 C^{11} , 124.52 C^{13} , 122.87 C^6 , 121.03 C^2 , 116.31 C^{12} , 116.09 C^{10} .

2.3.6. Synthesis of compound (6)

4'-Hydroxy-3-fluorochoalcone (**e**) (5.57 g, 23.01 mmol), 24 h. Yield: 3.18 g, 70%. *Anal. Calc.* for $[C_{90}H_{60}F_6N_3O_{12}P_3]$ (MW = 1582.36): found: C, 68.36; H, 3.85; N, 2.70%; requires; C, 68.31; H, 3.82; N, 2.66%. FT-IR (KBr, cm^{-1}): 3062 ν_{Ar-CH} , 2956 and 2917 $\nu_{Aliphatic-CH}$, 1666 $\nu_{C=O}$, 1606, 1577 and 1503 $\nu_{C=C}$, 1182 and 1207 $\nu_{P=N}$, 1282 ν_{P-N-P} , 953 ν_{P-O-C} . ^{31}P NMR(DMSO- d_6) δ/ppm : 7.97

68.31; H, 3.82; N, 2.66%. FT-IR (KBr, cm^{-1}): 3061 ν_{Ar-CH} , 2956 and 2920 $\nu_{Aliphatic-CH}$, 1665 $\nu_{C=O}$, 1607, 1581 and 1503 $\nu_{C=C}$, 1190 and 1206 $\nu_{P=N}$, 1271 ν_{P-N-P} , 953 ν_{P-O-C} . ^{31}P NMR (DMSO- d_6) δ/ppm : 7.99 (s). 1H NMR (DMSO- d_6) δ/ppm : 8.09 (12H, d, H^3), 7.91(6H, d, H^{11}), 7.75 (6H, d, H^7), 7.56–7.65 (12H, m, H^6 and H^{12}), 7.45 (6H, d, H^{13}), 7.26 (6H, s, H^9), 7.19 (12H, d, H^2), ^{13}C NMR (DMSO- d_6) δ/ppm : 187.95 C^5 , 161.66 C^{10} , 153.44 C^1 , 143.25 C^7 , 137.52–137.44 C^4 and C^8 , 135.18 C^{12} , 131.25 C^3 , 126.06 C^9 , 123.23 C^{13} , 121.18 C^6 , 117.91 C^{11} , 115.18 C^2 .

2.3.7. Synthesis of compound (7)

4'-Hydroxy-4-fluorochoalcone (**f**) (5.57 g, 23.01 mmol), 24 h. Yield: 3.86 g, 85%. *Anal. Calc.* for $[C_{90}H_{60}F_6N_3O_{12}P_3]$ (MW = 1582.36): found: C, 68.36; H, 3.85; N, 2.70%; requires; C, 68.31; H, 3.82; N, 2.66%. FT-IR (KBr, cm^{-1}): 3062 ν_{Ar-CH} , 2956 and 2917 $\nu_{Aliphatic-CH}$, 1666 $\nu_{C=O}$, 1606, 1577 and 1503 $\nu_{C=C}$, 1182 and 1207 $\nu_{P=N}$, 1282 ν_{P-N-P} , 953 ν_{P-O-C} . ^{31}P NMR(DMSO- d_6) δ/ppm : 7.97

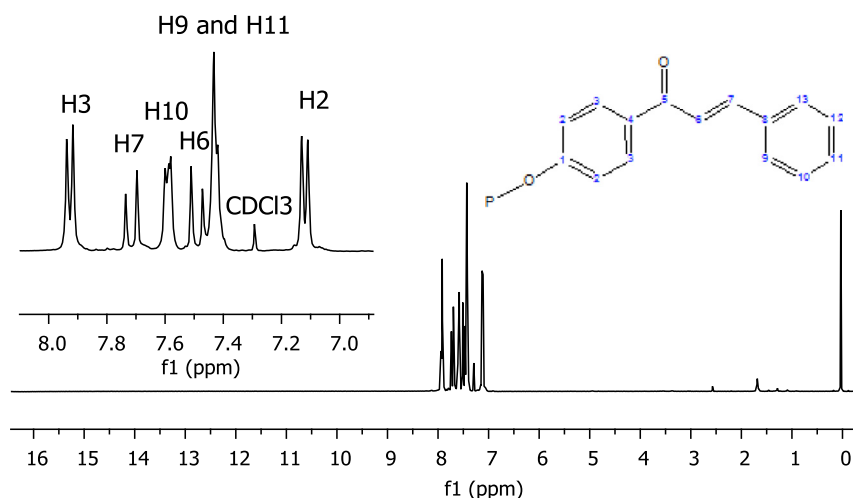


Fig. 1. 1H NMR spectrum of compound 2 (chloroform- d).

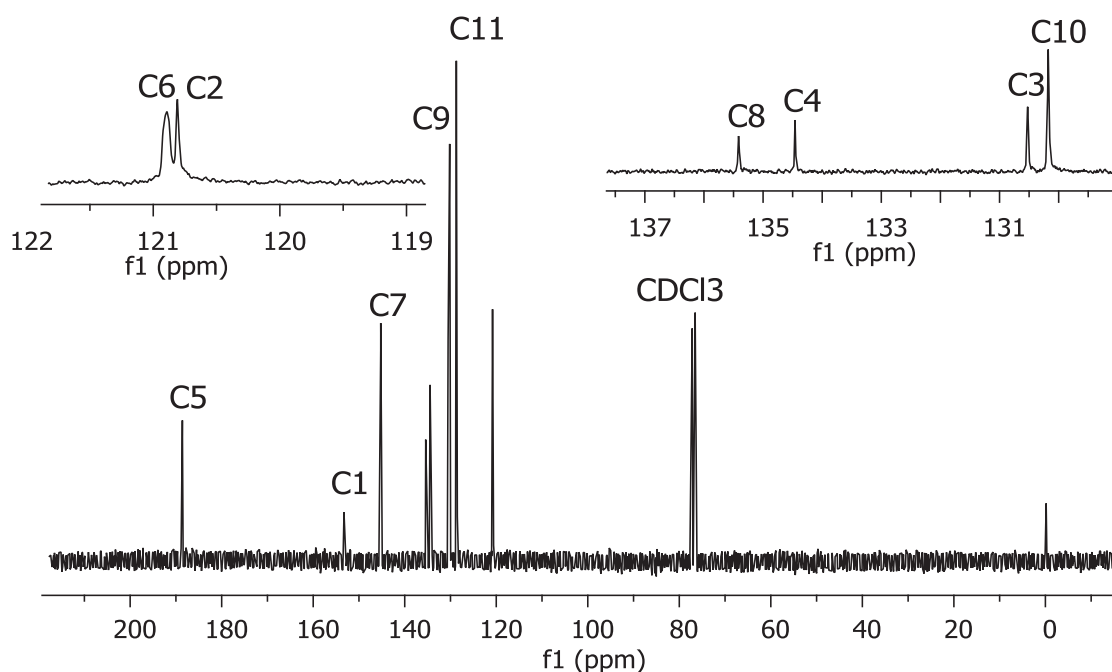


Fig. 2. ^{13}C NMR spectrum of compound 2 (chloroform- d).

(s). ^1H NMR (DMSO- d_6) δ /ppm: 7.99 (12H, d, H^3), 7.68 (6H, d, H^7), 7.59 (6H, d, H^6), 7.38 (12H, d, H^9), 7.23 (12H, d, H^2), 7.12 (12H, d, H^{10}), ^{13}C NMR (DMSO- d_6) δ /ppm: 188.66 C^5 , 160.49 C^{11} , 153.59 C^1 , 137.85 C^7 , 135.35 C^4 , 132.08 $\text{C}^{9,13}$, 130.46 C^3 , 129.84 C^8 , 122.85 C^2 , 121.05 C^6 , 116.32 $\text{C}^{10,12}$.

2.3.8. Synthesis of compound (8)

4'-Hydroxy-2-chlorochalcone (**g**) (5.95 g, 23.01 mmol), 18 h. Yield: 4.01 g, 83%. *Anal.* Calc. for $[\text{C}_{90}\text{H}_{60}\text{Cl}_6\text{N}_3\text{O}_{12}\text{P}_3]$ (MW = 1681.09): found: C, 64.36; H, 3.57; N, 2.53%; requires; C, 64.30; H, 3.60; N, 2.50%. FT-IR (KBr, cm^{-1}): 3064 $\nu_{\text{Ar-CH}}$, 2958 $\nu_{\text{Aliphatic-CH}}$, 1663 $\nu_{\text{C=O}}$, 1599, 1562 and 1500 $\nu_{\text{C=C}}$, 1182 and 1206 $\nu_{\text{P=N}}$, 1271 $\nu_{\text{P-N-P}}$, 946 $\nu_{\text{P-O-C}}$. ^{31}P NMR (CDCl_3) δ /ppm: 8.10 (s). ^1H NMR (CDCl_3) δ /ppm: 8.19 (6H, d, H^7), 7.94 (12H, d, H^3), 7.88 (6H, t, H^{13}), 7.50 (6H, d, H^6), 7.42 (6H, t, H^{11}), 7.33–7.36 (12H, m, H^{10} and H^{12}), 7.12 (12H, d, H^2), ^{13}C NMR (CDCl_3) δ /ppm: 188.66 C^5 , 153.57 C^1 , 141.12 C^7 , 135.61 C^8 , 135.32 C^4 , 132.90 C^9 , 131.40 C^{12} , 130.49 C^3 , 130.20 C^{10} , 127.99 C^{13} , 127.18 C^{11} , 123.66 C^6 , 121.09 C^2 .

2.3.9. Synthesis of compound (9)

4'-Hydroxy-2-methylchalcone (**h**) (5.48 g, 23.01 mmol), 15 h. Yield: 3.40 g, 76%. *Anal.* Calc. for $[\text{C}_{96}\text{H}_{78}\text{N}_3\text{O}_{12}\text{P}_3]$ (MW = 1558.58): found: C, 73.95; H, 5.10; N, 2.74%; requires; C, 73.98; H, 5.04; N, 2.70%. FT-IR (KBr, cm^{-1}): 3059 and 3016 $\nu_{\text{Ar-CH}}$, 2950 and 2923 $\nu_{\text{Aliphatic-CH}}$, 1662 $\nu_{\text{C=O}}$, 1596, 1570 and 1500 $\nu_{\text{C=C}}$, 1181 and 1204 $\nu_{\text{P=N}}$, 1295 $\nu_{\text{P-N-P}}$, 947 $\nu_{\text{P-O-C}}$. ^{31}P NMR (CDCl_3) δ /ppm: 7.97 (s). ^1H NMR (CDCl_3) δ /ppm: 8.11 (6H, d, H^7), 7.97 (12H, d, H^3), 7.80 (6H, d, H^{13}), 7.46 (6H, d, H^6), 7.20–7.33 (18H, m, H^{10} , H^{11} and H^{12}), 7.15 (12H, d, H^2), 2.38 (18H, s, H^{14}), ^{13}C NMR (CDCl_3) δ /ppm: 188.65 C^5 , 153.53 C^1 , 142.87 C^7 , 138.56 C^8 , 135.60 C^4 , 133.64 C^9 , 130.88 C^{12} , 130.44 C^{10} , 130.39 C^3 , 126.61 C^{13} , 126.38 C^{11} , 122.03 C^6 , 120.98 C^2 , 019.77 C^{14} .

2.3.10. Synthesis of compound (10)

4'-Hydroxy-3-methylchalcone (**k**) (5.48 g, 23.01 mmol), 15 h. Yield: 3.09 g, 69%. *Anal.* Calc. for $[\text{C}_{96}\text{H}_{78}\text{N}_3\text{O}_{12}\text{P}_3]$ (MW = 1558.58): found: C, 73.81; H, 5.01; N, 2.74%; requires; C, 73.98; H, 5.04; N, 2.70%. FT-IR (KBr, cm^{-1}): 3059 and 3016 $\nu_{\text{Ar-CH}}$, 2949 and 2921 $\nu_{\text{Aliphatic-CH}}$, 1659 $\nu_{\text{C=O}}$, 1602, 1574 and 1502 $\nu_{\text{C=C}}$, 1183 and 1205 $\nu_{\text{P=N}}$, 1269 $\nu_{\text{P-N-P}}$, 950 $\nu_{\text{P-O-C}}$. ^{31}P NMR (CDCl_3) δ /ppm: 7.97 (s). ^1H NMR (CDCl_3) δ /ppm: 7.93 (12H, d, H^3), 7.69 (6H, d, H^7), 7.49 (6H, d, H^6), 7.41 (6H, d, H^{13}), 7.29–7.34 (12H, m, H^9 and H^{12}), 7.26 (6H, d, H^{11}), 7.12 (12H, d, H^2), 2.41 (18H, s, H^{14}), ^{13}C NMR (CDCl_3) δ /ppm: 188.81 C^5 , 153.40 C^1 , 145.64 C^7 , 138.52 C^8 , 135.66 C^4 , 134.61 C^{10} , 131.54 C^9 , 130.36 C^3 , 129.44 C^{11} , 128.78 C^{12} , 125.93 C^{13} , 121.08 C^6 , 120.75 C^2 , 021.35 C^{14} .

2.3.11. Synthesis of compound (11)

4'-Hydroxy-4-nitrochalcone (**m**) (6.20 g, 23.01 mmol), 10 h. Yield: 3.01 g, 60%. *Anal.* Calc. for $[\text{C}_{90}\text{H}_{60}\text{N}_9\text{O}_{24}\text{P}_3]$ (MW = 1744.41): found: C, 62.01; H, 3.41; N, 7.30%; requires; C, 61.97; H, 3.47; N, 7.23%. FT-IR (KBr, cm^{-1}): 3062 and 3032 $\nu_{\text{Ar-CH}}$, 2947 and 2923 $\nu_{\text{Aliphatic-CH}}$, 1668 $\nu_{\text{C=O}}$, 1612, 1598, and 1515 $\nu_{\text{C=C}}$, 1193 and 1209 $\nu_{\text{P=N}}$, 1287 $\nu_{\text{P-N-P}}$, 955 $\nu_{\text{P-O-C}}$. ^{31}P NMR (DMSO- d_6) δ /ppm: 7.95 (s). ^1H NMR (DMSO- d_6) δ /ppm: 8.15 (12H, d, H^3), 8.09 (12H, d, H^{10}), 7.95–8.01 (18H, m, H^7 and H^9), 7.68 (6H, d, H^6), 7.22 (12H, d, H^2), ^{13}C NMR (DMSO- d_6) δ /ppm: 187.75 C^5 , 153.56 C^1 , 148.35 C^{11} , 141.77 C^8 , 141.30 C^7 , 134.93 C^4 , 131.33 C^{10} , 130.25 C^3 , 125.67 C^6 , 124.19 C^9 , 121.20 C^2 .

2.4. Dielectric properties

Dielectric studies on organic–inorganic hybrid material, which possess the excellent properties of both organic and inorganic compounds, are recently extensively investigated. Dielectric constant

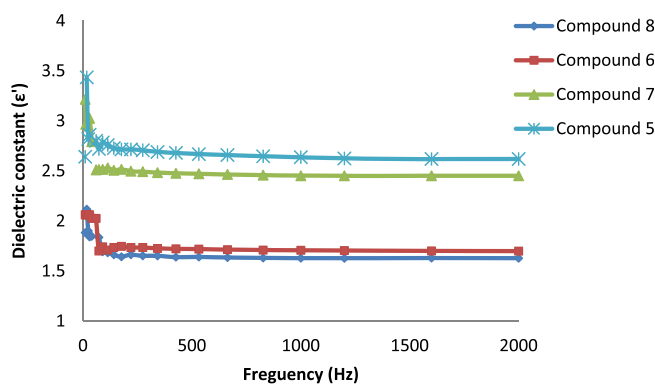


Fig. 3. The variation of real of the dielectric constant with frequency at room temperature.

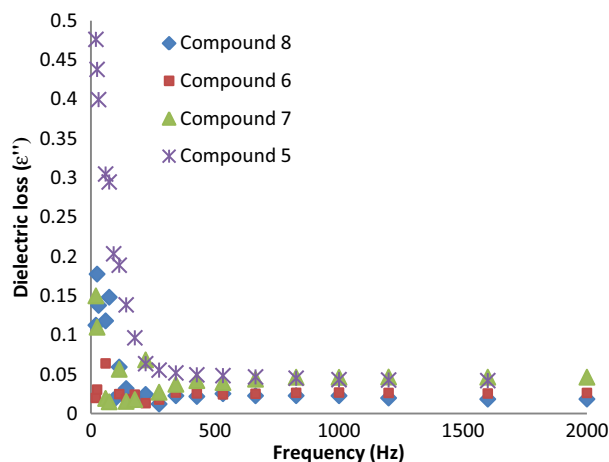


Fig. 4. The variation of the dielectric loss with frequency at room temperature.

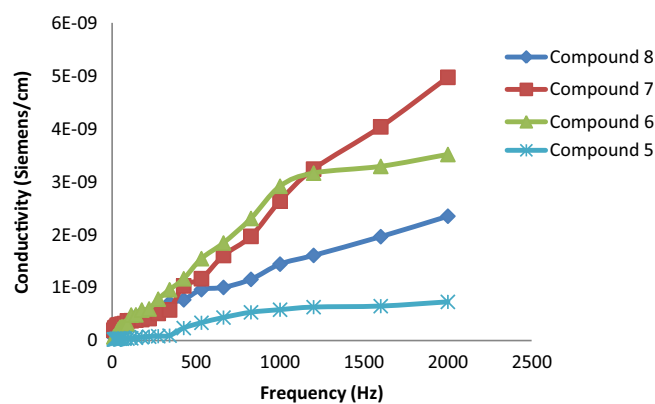


Fig. 5. The variation of the conductivity (σ) with frequency at room temperature.

and dielectric loss measurements were performed on pellet sample of compounds 5–8. The pellet was prepared from the pure powder sample through high-pressure of 5.0 MPa. The pressed-powder pellets deposited with carbon conducting glue were used for dielectric investigation. The capacitance of electrodes which was made by imitating the parallel-plate capacitor was measured with different frequencies. The dielectric constant and dielectric loss have been calculated using Eqs. (1) and (2):

$$\varepsilon' = Cp \frac{d}{\varepsilon_0 A} \quad (1)$$

$$\varepsilon'' = \varepsilon'' DF \quad (2)$$

where ε' is the dielectric constant, ε_0 is the dielectric constant of vacuum (8.854×10^{-12}), d is the thickness (m) and A is the area (m^2) of the sample and C is the capacitance (F) of test device. The frequency dependent dielectric was measured with frequency of 50 Hz to 2 kHz at room temperature.

2.4.1. Electrical properties

The ac electrical conductivity of the samples has been studied. Conductance (G_p) is a measure of how easily electricity flows along a certain path through an electrical element. The SI derived unit of conductance is the Siemens [61]. The frequency utilized in the study was from 50 Hz to 2 kHz. The measured conductance, G_p from 50 Hz up to 2 kHz was used to calculate ac conductivity, $\sigma(\omega)$ using the following expression:

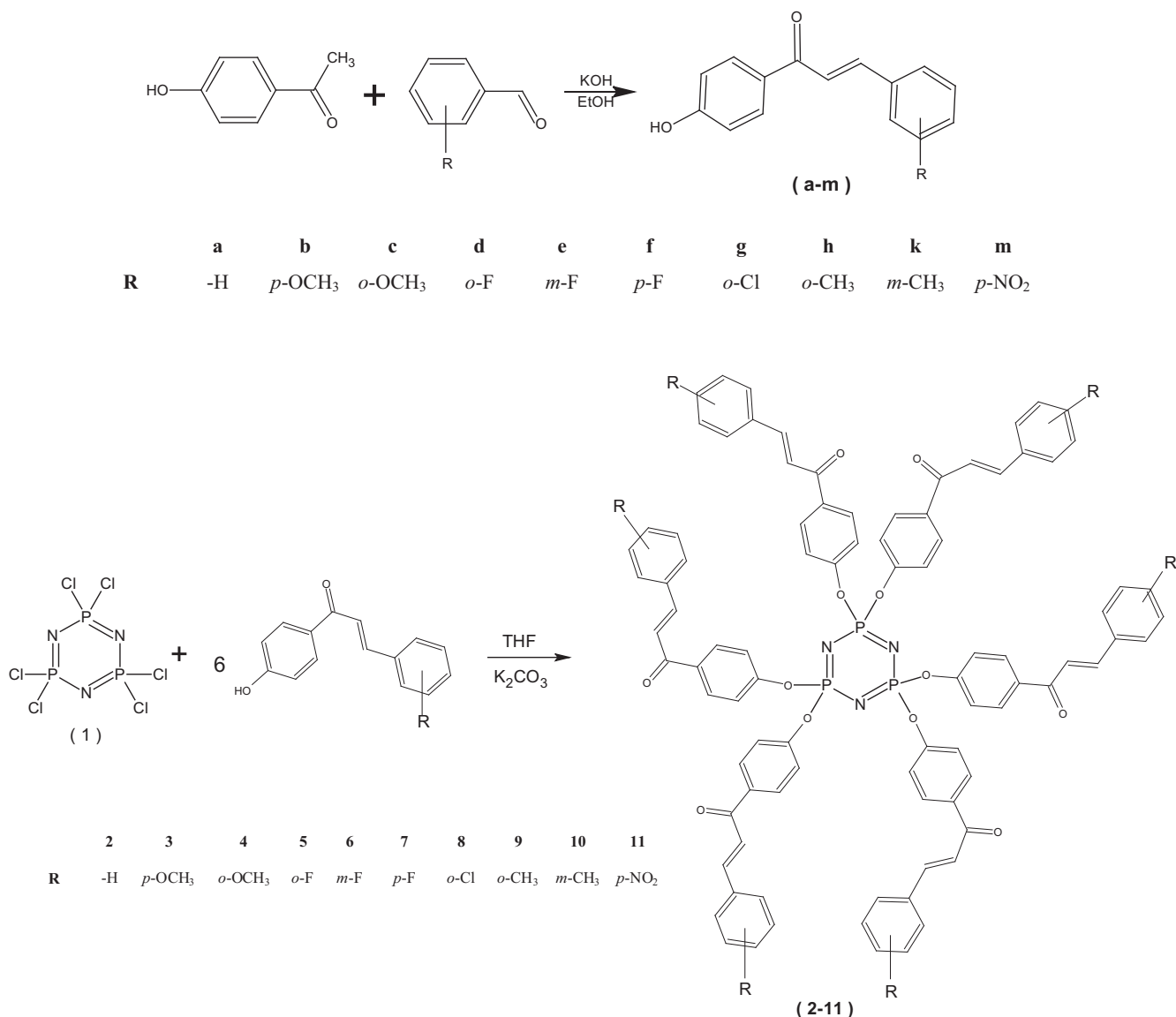
$$\sigma = G_p \frac{d}{A} \quad (3)$$

where d is the thickness of the sample and A is the cross-sectional area of the electrode. Fig. 5 shows the ac electrical conductivity of composite films.

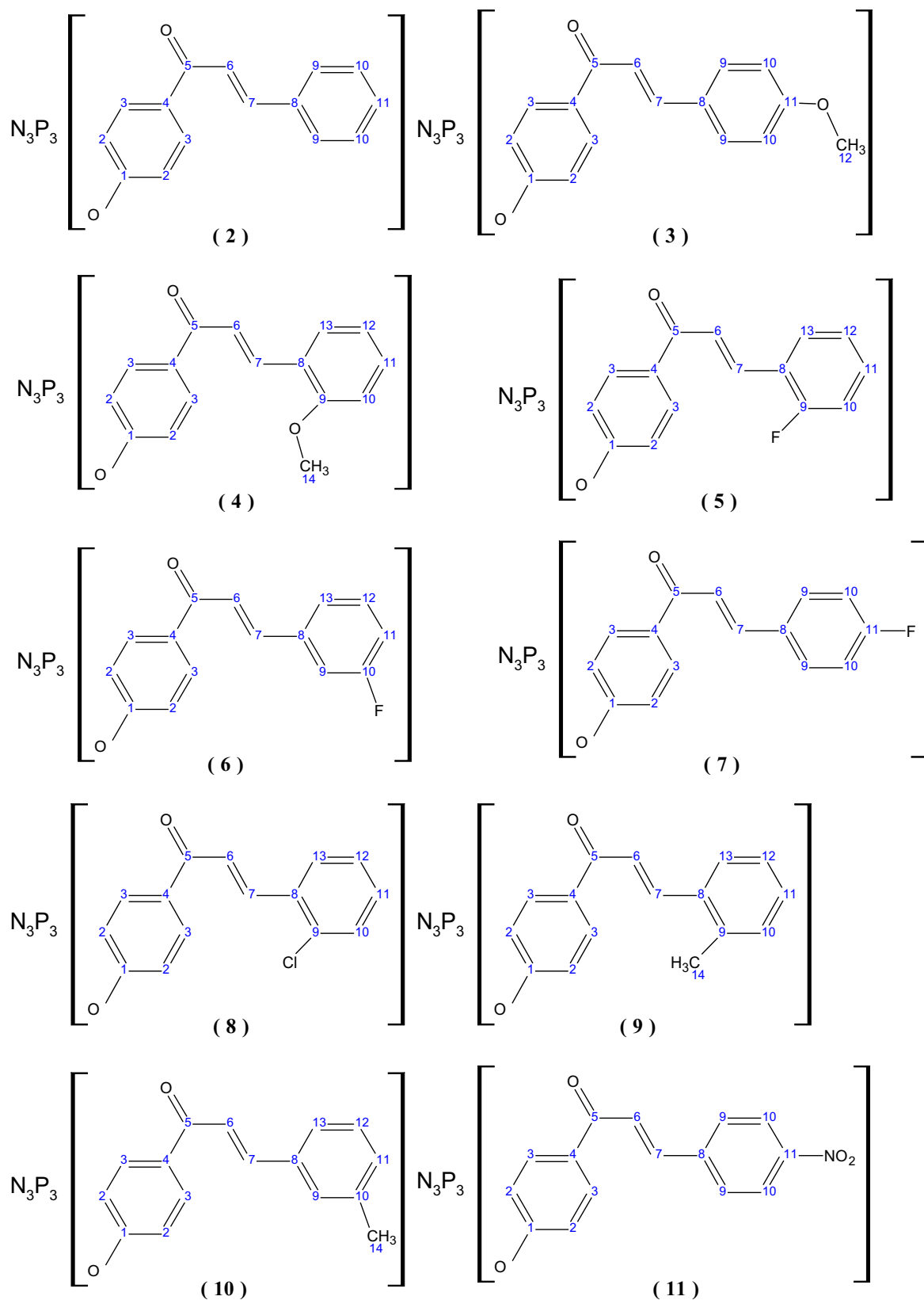
3. Results and discussion

The reactions of (1) with 6.1 equiv. of hydroxy chalcones in the presence of K_2CO_3 in acetone gave hexasubstituted products (2–11). The structures of the compounds were elucidated by FT-IR, ^1H , ^{13}C and ^{31}P NMR spectroscopy as well as by elemental analysis. All products were generally obtained in high yields. General presentation of the all reactions is shown in Scheme 1 and structures of the compounds 2–11 are shown in Scheme 2.

The characteristic stretching peaks in the FT-IR spectra of the phosphazenes have been assigned as in experimental section. The P=N stretching vibrations, which are observed between 1186 and 1193 cm^{-1} , are characteristic of cyclophosphazenes. These peaks are shifted to longer wavelengths for 2–11 than in (1), which appeared at 1218 cm^{-1} . The absence of the OH stretching vibration in the FT-IR spectra of 2–11 indicates that all hydrogen atoms of the OH groups have been replaced. In similarly, in the



Scheme 1. General presentation of the all reactions.



FT-IR spectra of **2–11**, the P–O–C stretching vibrations which were observed between 945 and 955 cm^{-1} and the C=O stretching vibrations which were observed between 1657 and 1666 cm^{-1} also indicate the hexasubstituted phosphazene compounds.

The NMR data of compounds **2–11** were given in experimental section. Example spectra (^1H and ^{13}C NMR spectra of **2**) was presented in Figs. 1 and 2. As expected, there is one peak in the ^{31}P NMR spectra of **2–11**. These single peaks which were observed

between 7.94 and 8.39 ppm in the ^{31}P NMR spectra of **2–11** confirm the structures of **2–11**.

The ^1H and ^{13}C NMR data also confirm the structures of **2–11** (Scheme 2). In the ^1H NMR spectra of **2–11**, the absence of the OH protons indicates the hexasubstituted phosphazene products. The aliphatic CH protons which were numbered as **6** and **7** in all compounds were observed between 7.46 and 7.68 ppm and 7.67 and 8.11 ppm respectively. The methyl protons for the compounds **3**, **4**, **9** and **10** were observed at 3.84, 3.87, 2.38 and 2.41 ppm respectively. The aromatic protons for all the compounds appear between 6.90 and 8.19 ppm.

The detailed ^{13}C NMR spectral data were given in experimental section. The carbonyl carbon atoms for **2–11** were observed at 1657, 1660, 1660, 1665, 1665, 1666, 1663, 1662, 1659 and 1666 cm^{-1} respectively. The methyl carbons for the compounds **3**, **4**, **9** and **10** were observed at 55.26, 50.46, 19.77 and 21.35 ppm respectively. For the compounds **2–11**, the aliphatic carbons which were numbered as **6** in all compounds were observed at 120.89, 118.45, 118.23, 122.87, 121.18, 121.05, 123.66, 122.03, 121.08 and 125.67 ppm respectively, while the aliphatic carbons which were numbered as **7** in all compounds were observed at 145.24, 145.07, 145.44, 137.83, 143.25, 137.85, 141.12, 142.87, 145.64 and 141.30 ppm respectively. Real and imaginary parts of the dielectric constant (ϵ' , ϵ''), ac conductivity (σ_{ac}) of phosphazenes containing chalcones have been calculated in wide frequency a range of 50 Hz to 2 kHz at room temperature. The graphical results of dielectric constant, dielectric loss and conductivity for samples (**5**, **6**, **7** and **8**) are presented in Figs. 3–5 respectively.

The frequency dependence of dielectric constant measurement shows that as the frequency increases, the dielectric constant drops sharply and drives to stability is shown Fig. 3. This behavior would be supported by the facts that atoms would be consistent with the direction change of AEF (alternating electric field) at low frequencies, while in higher frequencies, the dipole reversal can not keep up with the AEF frequency change, so the ϵ' decreases with the increase of frequency. The dielectric loss (ϵ''/ϵ') remains the similar trend with ϵ' . As seen Fig. 4 ϵ'' decreases with increasing frequency. The decrease in ϵ' and ϵ'' with increasing frequency indicated that the interfacial dipoles have less time to orient themselves in the direction of the alternate field [62]. As a results, the low-frequency region is attributed to the contribution of charge accumulation at the interface. At high frequencies, due to high periodic reversal of the field at the interface, the contribution of the charge carriers to the dielectric constant decreases with increasing frequency [63]. Results of the real part (ϵ') is maximum value showed Table 1.

Fig. 5 shows the variation of the conductivity (σ) with frequency at room temperature for compound **5–8**. The ac conductivity increases with increase of the frequency over a wide frequency range. The rise of conductivity upon increasing the frequency is a common respond for polymeric and semiconductor samples [64]. It is due to the tremendous increase of the mobility of charge carriers in the composite film. As shown in Fig. 5, there are two trends appeared, the first one (from 50 Hz up to 500 Hz) is frequency dependent conductivity and another (from 500 Hz up to 2 kHz) is frequency independent conductivity. The first trend is contributed by free charges available in the composite system whereas the second, which is frequency dependent conductivity, is due to trapped charges which is only active at higher frequency region [65,66]. The maximum conductivity has been found to be respectively 7.3×10^{-10} S/cm, 3.51×10^{-9} S/cm, 4.97×10^{-9} S/cm and 2.39×10^{-9} S/cm at the room temperature for **5**, **6**, **7** and **8**. These phosphazenes containing chalcones have conjugated structure and where there are many of π -electrons. Thus we believe that this conjugated structure causing electrical conductivity. The

Table 1

Results of the ϵ' , ϵ'' and σ are maximum value for compound **5–8**.

Compound	ϵ'	ϵ''	σ (S/cm)
(5)	2.61	0.042	7.3×10^{-10}
(6)	1.69	0.026	2.95×10^{-9}
(7)	2.45	0.046	5.01×10^{-9}
(8)	1.62	0.019	2.39×10^{-9}

conjugated double bonds of the compound create a decrease in the system's internal energy and apparently allow electron transfer for electronic conduction [67].

All of these parameters were found strong function of frequency and voltage especially in the inversion and depletion regions at low frequencies due to space charge polarization and charges at interface states. All of the results are compatible with literature [68,69].

4. Conclusion

In summary, the chalcone substituted cyclotriphosphazene compounds (**2–11**) were synthesized for the first time by using of $\text{K}_2\text{CO}_3/\text{acetone}$ system. All the compounds were generally obtained in high yields. Comprehensive studies of the AC conductivity, the dielectric properties of the compound **5–8** have been performed. The conductivity measurements were sensitivity between 10^{-9} and 10^{-10} Siemens. AC conductivity, the dielectric constant and the dielectric loss of the studied compound seem likely to be frequency dependent. The dielectric constant and dielectric loss of the sample decrease with increasing frequency. AC conductivity increase with increasing frequency.

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