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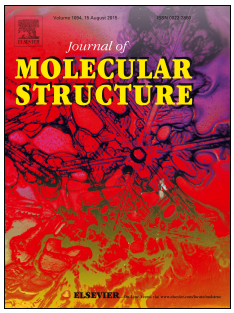

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Synthesis and characterization of 1,4-phenylenediamine derivatives containing hydroxyl and cyclotriphosphazene as terminal group

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ABSTRACT

A series of compounds with two Schiff base linking units and four different substituents (heptyl, dodecyl, methoxy and chloro) have been successfully synthesized. Further reactions form new monosubstituted cyclotriphosphazene based molecules with different substituents. These compounds were characterized using FT-IR (Fourier Transform Infrared), NMR (Nuclear Magnetic Resonance) and CHN elemental analysis. The transition mesophase(s) of these compounds were determined using POM (Polarized Optical Microscope) and DSC (Differential Scanning Calorimetry). Two compounds with heptyl and dodecyl substituents were found to be mesogenic with smectic C phases while monosubstituted cyclotriphosphazene compounds of the same substituents (heptyl and dodecyl chains) were also found to be mesogenic. Cyclotriphosphazene compounds with heptyl chain shows smectic C and nematic phases while compound with dodecyl chain shows only the nematic phase. However, compounds with methoxy and chloro substituents were found to be non-mesogenic.

KEYWORDS: Cyclotriphosphazene, Schiff base, mesogenic, nematic, smectic C

INTRODUCTION

The study of liquid crystal materials has expanded greatly over the years. Even though a large number of liquid crystal compounds have been synthesized and characterized, not many cyclotriphosphazene liquid crystal molecules have been reported. Liquid crystal is a state between solid (crystal) and liquid (isotropic) states. Liquid crystal may flow like a liquid but its molecule has some solid properties and is oriented in a crystal-like way. The study of LC properties began in 1888 when an Austrian botanist, Friedrich Reinitzer discovered a material known as cholesteryl benzoate with two distinct melting points. Upon heating, the solid changes into a hazy liquid and further heating transformed it into a clear liquid. This finding started the discovery of a new phase of matter called the liquid crystal phase [1].

The phosphorus-nitrogen chemistry, in particular the study of cyclotriphosphazenes started since the nineteenth century but has been intensively investigated only in the mid 1950's [2]. Cyclotriphosphazene is a ring compound consisting of alternating phosphorus and nitrogen atoms with two substituents attached to the phosphorus atoms (Figure 1).

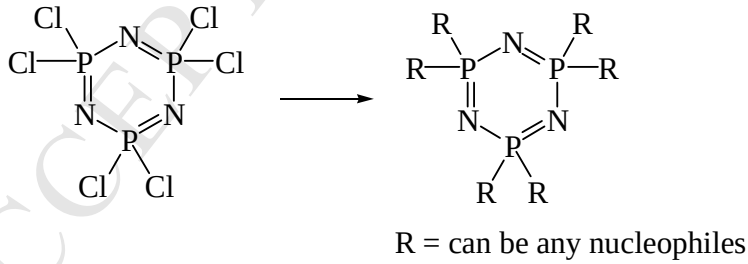


Figure 1. Structure of cyclotriphosphazene.

Much attention has been focused on these interesting compounds because they consist of inorganic backbones as well as organic side-chains. They have remarkable

chemical stability and synthetic versatility which enables the introduction of any side group, R on phosphorus [3]. Previous studies reported that substituents such as $–NH_2$, -OR, $-OC_6H_5$ or fluorinated derivatives are able to enhance the oxidative and thermal stabilities [4]. Allcock and Klingenberg (1995) reported the aromatic azo phosphazene liquid crystals, investigating the effect of the substituents on the aromatic unit, the function of the chain length and different phosphazene skeletal structures [5]. Schiff base unit when attached to the cyclotriphosphazene core were reported to have variety of applications as flame resistance, biomedicine, semiconductors, dyes and catalysis [6-9].

This research work involved the synthesis and characterization of new compounds having two Schiff base linking units with different terminal substituents. These intermediates were further attached to the cyclotriphosphazene core through mono substitution reaction. The aim is to determine the liquid crystal properties of these cyclotriphosphazene compounds. In order to avoid complications from varieties of terminal group associations, the main variables that will be studied are the effect of the chain length and the type of terminal substituents towards the liquid crystal properties.

MATERIALS AND METHODS

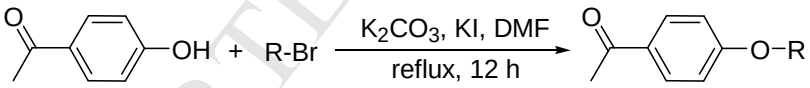
CHEMICALS

The chemicals used in this study are listed as follows: 1-bromoheptane (MERCK Schuchardt OHG), 1-bromododecane (MERCK Schuchardt OHG), 4-hydroxybenzaldehyde (MERCK Schuchardt OHG), 1,4-phenylenediamine (MERCK Schuchardt OHG), 4-chlorobenzaldehyde (MERCK Schuchardt OHG), 4-methoxybenzaldehyde (MERCK Schuchardt OHG), methanol (QREC (ASIA) Sdn Bhd), *N*,*N*-dimethylformamide (QREC

(ASIA) Sdn Bhd), potassium carbonate (QREC (ASIA) Sdn Bhd), potassium iodide (MERCK Schuchardt OHG), anhydrous sodium sulphate (MERCK Schuchardt OHG), *n*-hexane (QREC (ASIA) Sdn Bhd), ethyl acetate (BDH Laboratory Supplies Poole), dichloromethane (QREC (ASIA) Sdn Bhd), tetrahydrofuran (MERCK Schuchardt OHG) and phosphonitrilic chloride trimer (SIGMA-ALDRICH Co.).

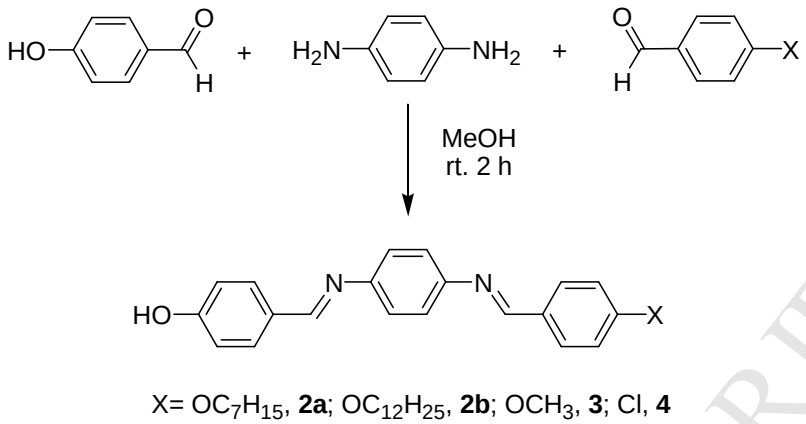
EXPERIMENTAL

Compounds **1a-b** were synthesized using the alkylation reaction of *p*-hydroxybenzaldehyde (Scheme 1). Further reaction of phenyldiamine with some *para* substituted benzaldehyde afforded compounds **2a-b, 3** and **4** (Scheme 2). Reaction of cyclotriphosphazene ring with 4-hydroxybenzaldehyde gave compound **5** (Scheme 3) which was used for further reaction to yield the final compounds **6a**, **6b**, **7** and **8** (Scheme 4)



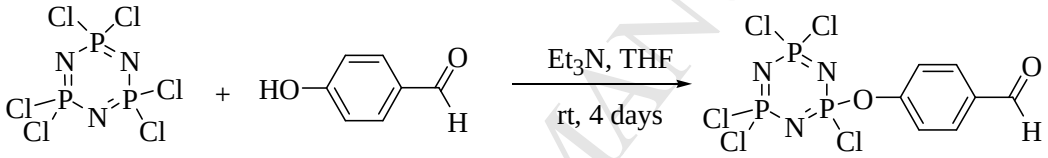
R= C_7H_{15}, **1a**; $C_{12}H_{25}$, **1b**

Scheme 1. Alkylation reaction of intermediates **1a** and **1b** [10].

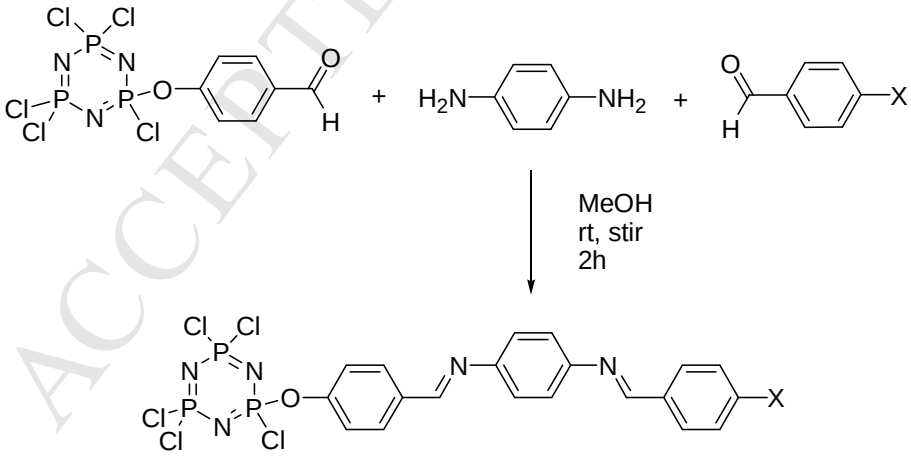


X= OC_7H_{15}, **2a**; $OC_{12}H_{25}$, **2b**; OCH_3, **3**; Cl, **4**

Scheme 2. Condensation reaction of compounds **2a**, **2b**, **3** and **4** [11].



Scheme 3. Formation of monosubstituted cyclotriphosphazene, **5** [12].



X= OC_7H_{15}, **6a**; $OC_{12}H_{25}$, **6b**; OCH_3, **7**; Cl, **8**

Scheme 4. Condensation reaction of compound **6a**, **6b**, **7** and **8** [13].

(**1a**) Synthesis of 4-heptyloxybenzaldehyde

4-hydroxybenzaldehyde (6.11 g, 0.05 mol) and 1-bromoheptane (8.95 g, 0.05 mol) were dissolved in *N*,*N*-dimethylformamide, DMF (10 mL), separately. Both solutions were mixed in a 100 mL round bottom flask. Potassium carbonate (10.37 g, 0.06 mol) and potassium iodide (0.83 g, 0.005 mol) were added into the mixture and was refluxed for 12 hours. The reaction was monitored using TLC. Upon completion, the mixture was poured into 250 mL cold water and was extracted using ethyl acetate. The organic layers were collected and dried in anhydrous sodium sulphate. The product was filtered, evaporated and dried in vacuum oven overnight. The same method was used to synthesis **1b**. Yield: 7.89 g (71.73 %), light-yellow oil. FT-IR (cm^{-1}): 2928 and 2858 (asymmetrical and symmetrical Csp^3-H stretching), 2769 (H-CO, aldehydic stretching), 1691 (C=O stretching), 1600 (C=C stretching), 1252 (C-O stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 9.86 (s, 1H), 7.81 (d, *J*=10.0 Hz, 2H), 7.00 (d, *J*=10.0 Hz, 2H), 3.94 (t, *J*=7.5 Hz, 2H), 1.66-1.69 (m, 2H), 1.32-1.36 (m, 2H), 1.20-1.24 (m, 6H), 0.82 (t, *J*=7.5 Hz, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 190.20, 163.60, 131.44, 129.55, 114.44, 67.86, 31.28, 28.59, 28.57, 25.44, 22.09, 13.59.

(**1b**) 4-dodecyloxybenzaldehyde

Yield: 10.79 g (74.38 %), dark-yellow oil. FT-IR (cm^{-1}): 2922 and 2855 (asymmetrical and symmetrical Csp^3-H stretching), 2733 (H-CO, aldehydic stretching), 1688 (C=O stretching), 1600 (C=C stretching), 1255 (C-O stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 9.83 (s, 1H), 7.80 (d, *J*=10.0 Hz, 2H), 7.02 (d, *J*=10.0 Hz, 2H), 3.98 (t, *J*=7.5 Hz, 2H), 1.66-1.69 (m, 2H), 1.33-1.35 (m, 2H), 1.12-1.28 (m, 16H), 0.80 (t, *J*=7.5 Hz, 3H). ^{13}C-

NMR (125 MHz, DMSO-d_6) δ, ppm: 190.76, 163.58, 131.59, 129.50, 114.60, 67.88, 31.34, 29.12, 29.09, 29.07, 29.05, 28.82, 28.79, 28.52, 25.43, 22.10, 13.74.

(**2a**) Synthesis of 4-({4-[(4-heptyloxybenzyliden)amino]phenylimino}methyl) phenol

A mixture of 4-hydroxybenzaldehyde (0.50 g, 4.10 mmol) and 1,4-phenylenediamine (0.44 g, 4.10 mmol) in methanol (15 mL) were placed in a round bottom flask. 4-heptyloxybenzaldehyde (0.90 g, 4.10 mmol) was added into the mixture and the reaction mixture was stirred at room temperature for two hours. The reaction progress was monitored by TLC. Upon completion, the mixture was cooled in ice water and the precipitate formed was filtered and dried. The crude was recrystallized using methanol. The same method was used to synthesis **2b**, **3** and **4**. Yield = 1.29 g (76.09%), mp: 115.2-117.7 °C, yellow powder. FT-IR (cm^{-1}): 3188 (O-H stretching), 3069 (Csp^2-H stretching), 2925 and 2861 (asymmetrical and symmetrical Csp^3-H stretching), 1600 (C=N stretching), 1511 (C=C stretching), 1249 (C-O stretching), 1163 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 8.57 (s, 1H), 8.50 (s, 1H), 7.87 (d, *J*=10.0 Hz, 2H), 7.78 (d, *J*=5.0 Hz, 2H), 7.27 (d, *J*=10.0 Hz, 2H), 7.25 (d, *J*=10.0 Hz, 2H), 7.05 (d, *J*=10.0 Hz, 2H), 6.90 (d, *J*=5.0 Hz, 2H), 4.08 (t, *J*=5.0 Hz, 2H), 1.75-1.78 (m, 2H), 1.43-1.48 (m, 2H), 1.31-1.39 (m, 6H), 0.89 (t, *J*=7.5 Hz, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 161.56, 160.64, 158.83, 158.73, 149.43, 149.40, 133.32, 132.46, 130.43, 130.29, 121.66, 121.57, 115.70, 114.91, 68.02, 31.09, 28.61, 28.25, 25.36, 21.84, 13.66. CHN elemental analysis: Calculated for $C_{27}H_{30}N_2O_2$: C: 78.23 %, H: 7.29 %, N: 6.76 %; Found: C: 78.01 %, H: 7.27 %, N: 6.75 %.

(**2b**) 4-({4-[(4-dodecyloxybenzylidene)amino]phenylimino}methyl) phenol

Yield = 1.33 g (67.02%), mp: 120.1-122.8°C, yellow powder. FT-IR (cm^{-1}): 3277 (O-H stretching), 3066 (Csp^2-H stretching), 2917 and 2852 (asymmetrical and symmetrical Csp^3-H stretching), 1598 and 1576 (C=N stretching), 1511 (C=C stretching), 1250 (C-O stretching), 1170 (C-N stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 8.56 (s, 1H), 8.50 (s, 1H), 7.87 (d, *J*=10.0 Hz, 2H), 7.78 (d, *J*=5.0 Hz, 2H), 7.27 (d, *J*=10.0 Hz, 2H), 7.25 (d, *J*=10.0 Hz, 2H), 7.05 (d, *J*=10.0 Hz, 2H), 6.90 (d, *J*=5.0 Hz, 2H), 4.08 (t, *J*=7.5 Hz, 2H), 1.77-1.74 (m, 2H), 1.43-1.45 (m, 2H), 1.28-1.36 (m, 16H), 0.87 (t, *J*=7.5 Hz, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 161.46, 160.56, 158.83, 158.62, 149.43, 149.40, 134.95, 133.37, 130.43, 130.27, 121.64, 121.57, 115.70, 114.90, 68.01, 31.16, 28.88, 28.86, 28.82, 28.73, 28.70, 28.60, 28.52, 25.38, 21.90, 13.67. CHN elemental analysis: Calculated for $C_{32}H_{40}N_2O_2$: C: 79.30 %, H: 8.32 %, N: 5.78 %. Found: C: 79.29 %, H: 8.32 %, N: 5.77 %.

(**3**) 4-({4-[(4-methoxybenzyliden)amino]phenylimino}methyl)phenol

Yield: 1.02 g (75.38%), mp: 175.1-178.4 °C, yellow powder. FT-IR (cm^{-1}): 3163 (O-H stretching), 3023 (Csp^2-H stretching), 2879 (Csp^3-H stretching), 1594 (C=N stretching), 1511 (C=C stretching), 1252 (C-O stretching), 1160 (C-N stretching). ^{1}H NMR (500 MHz, DMSO-d_6) **δ**, ppm: 8.59 (s, 1H), 8.51 (s, 1H), 7.90 (d, *J*=5.0 Hz, 2H), 7.78 (d, *J*=10.0 Hz, 2H), 7.30 (d, *J*=5.0 Hz, 2H), 7.27 (d, *J*=10.0 Hz, 2H), 7.08 (d, *J*=10.0 Hz, 2H), 6.88 (d, *J*= 10.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) **δ**, ppm: 161.84, 160.51, 159.13, 159.09, 149.26, 149.23, 134.63, 133.32, 131.58, 130.39, 121.85, 121.75, 115.62,

114.25, 55.38. CHN elemental analysis: Calculated for $C_{21}H_{18}N_2O_2$: C: 76.34%, H: 5.49%, N: 8.48%. Found: C: 76.11%, H: 5.45%, N: 8.46%.

(**4**) 4-({4-[(chlorobenzyliden)amino]phenylimino}methyl) phenol

Yield: 0.95 g (75.61%), mp: 178.2-180.7 °C, yellow powder. FT-IR (cm^{-1}): 3185 (O-H stretching), 3026 (Csp^2-H stretching), 2882 (Csp^3-H stretching), 1600 (C=N stretching), 1493 (C=C stretching), 1276 (C-O stretching), 1163 (C-N stretching), 824 (C-Cl bending). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm; 8.71 (s, 1H), 8.51 (s, 1H), 7.97 (d, *J*=10.0 Hz, 2H), 7.78 (d, *J*=10.0 Hz, 2H), 7.60 (d, *J*=10.0 Hz, 2H), 7.37 (d, *J*=10.0 Hz, 2H), 7.27 (d, *J*=10.0 Hz, 2H), 6.88 (d, *J*= 10.0 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ, ppm: 160.52, 159.14, 158.92, 149.27, 149.12, 135.98, 134.92, 133.43, 130.58, 130.25, 128.97, 122.12, 121.75, 115.62. CHN elemental analysis: Calculated for $C_{20}H_{15}N_2OCl$: C: 71.75 %, H: 4.52 %, N: 8.37 %. Found: C: 71.60 %, H: 4.50 %, N: 8.35 %.

(**5**) Synthesis of monosubstituted cyclotriphosphazene benzaldehyde

4-hydroxybenzaldehyde (3.54 g, 0.029 mol) and triethylamine (2.93 g, 0.029 mol) were dissolved in tetrahydrofuran, THF (10 mL). The mixture was cooled to 0 °C in an ice bath and was stirred vigorously for an hour. Then, phosphonitrilic chloride trimer (10.0 g, 0.029 mol) which was dissolved in THF (10 mL) was added dropwise into the mixture. A white salt began to precipitate within few minutes. After three hours at 0 °C, the reaction was allowed to attain at room temperature and was continued to stir for an additional 93 hours. The reaction was monitored using TLC. Upon completion, the mixture was filtered to remove the triethylamine hydrochlroride salt. THF solution was removed by rotary

evaporation. The residue was then dissolved in dichlromethane and washed several times with distilled water. The organic layer was collected and the dichlromethane solution was removed by rotary evaporation. The yellow oil residue was purified using column chromatography. Yield: 8.56 g (68.15%), light yellow oil. FT-IR (cm^{-1}): 1706 (C=O stretching), 1500 (C=C stretching), 1238 (C-O stretching), 1176 (P=N stretching), 977 (P-O-C stretching). ^{1}H-NMR (500 MHz, $CDCl_3$) δ, ppm: 10.00 (s, 1H) , 7.94 (d, *J*=10.0 Hz, 2H), 7.43 (d, *J*=5.0 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ, ppm: 190.53, 153.57, 134.65, 131.69, 131.67, 122.16, 122.12. ^{31}P-NMR (500 MHz, $CDCl_3$) δ, ppm: 22.48 (d, *J*=155.0 Hz, 2P), 11.71 (t, *J*=155.0 Hz, 1P).

(**6a**) Synthesis of *N*-(4-heptyloxybenzylidene)-*N'*-[4-(2,4,4,6,6-pentachloro-2λ^5,4λ^5,6λ^5-[1,3,5,2,4,6]-triazatriphosphinin-2-yloxy)benzaldehydene] benzene-1,4-diamine

A mixture of monosubstituted cyclotriphosphazene compound, **5** (1.00 g, 2.31 mmol) and 1,4-phenylenediamine (0.25 g, 2.31 mmol) in methanol (15 mL) was placed in a round bottom flask. Then, 4-heptyloxybenzaldehyde (0.51 g, 2.31 mmol) was added dropwise into the mixture. The reaction was stirred at room temperature for two hours. The reaction was monitored by TLC. Upon completion, the mixture was cooled in ice water and the precipitate formed was filtered and dried. The crude was recrystallized using methanol. The same method was used to synthesis **6b**, **7** and **8**. Yield: 1.15 g (69.09%), mp: 118.1-120.8 ^{o}C, yellow powder. FT-IR (cm^{-1}): 2922 and 2857 (asymmetrical and symmetrical Csp^3-H stretching), 1605 (C=N stretching), 1510 (C=C stretching), 1249 (C-O stretching), 1187 (P=N stretching), 1169 (C-N stretching), 1013 (P-O-C stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 8.68 (s, 1H), 8.58 (s, 1H), 7.96 (d, *J*=5.0 Hz, 2H), 7.88 (d, *J*=10.0 Hz,

2H), 7.53 (d, *J*=5.0 Hz, 2H), 7.34 (d, *J*=10.0 Hz, 2H), 7.30 (d, *J*=15.0 Hz, 2H), 7.06 (d, *J*=10.0 Hz, 2H), 4.07 (t, *J*=7.5 Hz, 2H), 1.74-1.77 (m, 2H), 1.43-1.45 (m, 2H), 1.31-1.36 (m, 6H), 0.89 (t, *J*=5.0 Hz, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 161.97, 160.90, 160.05, 159.55, 150.34, 149.46, 136.80, 135.53, 131.72, 130.86, 129.21, 122.36, 122.24, 115.51, 68.43, 31.62, 29.10, 28.79, 25.88, 22.40, 14.24. ^{31}P-NMR (500 MHz, DMSO-d_6) δ, ppm: 23.24 (d, *J*=150.0 Hz, 2P), 12.45 (t, *J*=155.0 Hz, 1P). CHN elemental analysis: Calculated for $C_{27}H_{29}N_5O_2Cl_5P_3$: C: 44.68 %, H: 4.03 %, N: 9.65 %. Found: C: 44.62 %, H: 4.03 %, N: 9.66 %.

(**6b**) *N*-(4-dodecyloxybenzylidene)-*N*'-[4-(2,4,4,6,6-pentachloro-2λ^5,4λ^5,6λ^5-[1,3,5,2,4,6]-triazatriphosphinin-2-yloxy)benzaldehydene] benzene-1,4-diamine

Yield: 1.23 g (67.43%), mp: 121.7-124.1 ºC, yellow powder. FT-IR (cm^{-1}): 2918 and 2853 (asymmetrical and symmetrical C*sp*^{3}-H stretching), 1608 (C=N stretching), 1510 (C=C stretching), 1252 (C-O stretching), 1194 (P=N stretching), 1169 (C-N stretching), 1024 (P-O-C stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 8.68 (s, 1H), 8.58 (s, 1H), 7.95 (d, *J*=10.0 Hz, 2H), 7.88 (d, *J*=10.0 Hz, 2H), 7.53 (d, *J*=5.0 Hz, 2H), 7.34 (d, *J*=10.0 Hz, 2H), 7.30 (d, *J*=10.0 Hz, 2H), 7.06 (d, *J*=5.0 Hz, 2H), 4.07 (t, *J*=5.0 Hz, 2H), 1.74-1.76 (m, 2H), 1.43-1.45 (m, 2H), 1.27-1.35 (m, 16H), 0.87 (t, *J*=5.0 Hz, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 162.80, 161.98, 160.05, 159.54, 150.31, 149.43, 136.85, 135.47, 131.72, 130.86, 129.05, 122.35, 122.24, 115.34, 68.41, 31.69, 29.41, 29.38, 29.35, 29.25, 29.12, 29.11, 29.06, 25.88, 22.44, 14.24. ^{31}P-NMR (500 MHz, DMSO-d_6) δ, ppm: 23.55 (d, *J*=155.0 Hz, 2P), 12.75 (t, *J*=155.0 Hz, 1P). CHN elemental analysis: Calculated for

$C_{32}H_{39}N_5O_2Cl_5P_3$: C: 48.29 %, H: 4.94 %, N: 8.80 %. Found: C: 48.22 %, H: 4.93 %, N: 8.81 %.

(**7**) *N*-(4-methoxybenzylidene)-*N'*-[4-(2,4,4,6,6-pentachloro-2λ^5,4λ^5,6λ^5-[1,3,5,2,4,6]-triaza triphosphinin-2-yloxy)benzaldehydene] benzene-1,4-diamine

Yield: 1.07 g (72.51%), mp: 207.3-210.5 ºC, yellow powder. FT-IR (cm^{-1}): 2839 (C*sp*^{3}-H stretching), 1601 (C=N stretching), 1503 (C=C stretching), 1296 (C-O stretching), 1198 (P=N stretching), 1169 (C-N stretching), 980 (P-O-C stretching). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 8.90 (s, 1H), 8.69 (s, 1H), 7.96 (d, *J*=5.0 Hz, 2H), 7.54 (d, *J*=5.0 Hz, 2H), 7.53 (d, *J*=5.0 Hz, 2H), 7.36 (d, *J*=15.0 Hz, 2H), 7.30 (d, *J*=5.0 Hz, 2H), 7.08 (d, *J*= 15.0 Hz, 2H), 3.90 (s, 3H). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 160.38, 160.06, 159.29, 159.24, 149.82, 149.28, 136.06, 133.13, 131.42, 130.30, 128.81, 122.01, 121.91, 112.01, 55.78. ^{31}P-NMR (500 MHz, DMSO-d_6) δ, ppm: 22.50 (d, *J*=150.0 Hz, 2P), 12.11 (t, *J*=170.0 Hz, 1P). CHN elemental analysis: Calculated for $C_{21}H_{17}N_5O_2Cl_5P_3$: C: 39.31 %, H: 2.67 %, N: 10.92 %. Found: C: 39.09 %, H: 2.64 %, N: 10.87 %.

(**8**) *N*-(4-chlorobenzylidene)-*N'*-[4-(2,4,4,6,6-pentachloro-2λ^5,4λ^5,6λ^5-[1,3,5,2,4,6]-triazatri phosphinin-2-yloxy)benzaldehydene] benzene-1,4-diamine

Yield: 0.96 g (64.61%), mp: 220.5-223.0 ºC, orange powder. FT-IR (cm^{-1}): 1612 (C=N stretching), 1492 (C=C stretching), 1274 (C-O stretching), 1205 (P=N stretching), 1180 (C-N stretching), 1075 (P-O-C stretching), 842 (C-Cl bending). ^{1}H-NMR (500 MHz, DMSO-d_6) δ, ppm: 8.71 (s, 1H), 8.69 (s, 1H), 7.97 (d, *J*=10.0 Hz, 2H), 7.95 (d, *J*=10.0 Hz, 2H), 7.60 (d, *J*=10.0 Hz, 2H), 7.54 (d, *J*=5.0 Hz, 2H), 7.38 (d, *J*=5.0 Hz, 2H), 7.37 (d, *J*= 5.0 Hz,

2H,). ^{13}C-NMR (125 MHz, DMSO-d_6) δ, ppm: 160.05, 158.88, 158.77, 154.48, 149.49, 148.90, 136.04, 134.94, 131.44, 130.23, 128.95, 128.64, 122.11, 122.02. ^{31}P-NMR (500 MHz, DMSO-d_6) δ, ppm: 22.54 (d, *J*=155.0 Hz, 2P), 11.74 (t, *J*=155.0 Hz, 1P). CHN elemental analysis: Calculated for $C_{20}H_{14}N_5O_2Cl_6P_3$: C: 37.18 %, H: 2.18 %, N: 10.84 %. Found: C: 37.12 %, H: 2.20 %, N: 10.83 %.

RESULTS AND DISCUSSION

FT-IR spectral discussion

The research works involved the alkylation reaction of *p*-hydroxybenzaldehyde with alkylbromide in the presence of potassium carbonate and potassium iodide to produce intermediates **1a** and **1b** (Scheme 1).The IR data for intermediates **1a** and **1b** showed the absorption bands at 2890 and 2920 cm^{-1} for the symmetrical and asymmetrical C-H (sp^3) stretching. The band at 2730 cm^{-1} was assigned for the aldehydic C-H stretching while bands at 1689, 1602 and 1253 cm^{-1} were attributed to the C=O, C=C and C-O stretching, respectively. No broad absorption band for the O-H stretching (3300 cm^{-1}) was observed which confirmed that the insertion of the alkyl group into the benzaldehyde was successful.

Further reaction of *p*-phenylenediamine with intermediates **1a** (heptyl chain), **1b** (dodecyl chain) and two other benzaldehydes (methoxy and chloro) produced four Shiff base compounds (**2a**, **2b**, **3** and **4**) with different substituents (Scheme 2). All compounds showed a broad absorption of the O-H stretching in the region of 3220-3560 cm^{-1}. The absorption bands for C=N, C=C and C-N stretching were observed at 1600, 1500 and 1160 cm^{-1} respectively. Compounds **2a** and **2b** showed strong absorption bands at 2850 and 2980 cm^{-1} due to the symmetrical and asymmetrical Csp^3-H stretching of the heptyl and dodecyl

chains [14]. Compound 3 showed only the Csp^3-H stretching at 2879 cm^{-1}. Absorptions were observed at 1250 cm^{-1} for C-O stretching of compounds **2a**, **2b** and **3.** A band at 824 cm^{-1} was assigned for C-Cl stretching in compound **4**. No absorption bands of the aldehydic C-H stretching in all the intermediates but instead all intermediates showed the C=N stretching at 1612 cm^{-1} which confirmed the formation of the Schiff base moiety.

The monosubstituted cyclotriphosphazene compound, **5** has been synthesized by substitution reaction of *p*-hydroxybenzaldehyde with cyclotriphosphazene as shown in Scheme 3. The IR spectrum of monosubstituted cyclotriphosphazene, **5** showed the absorptions 1706, 1500 and 1238 cm^{-1} for the C=O, C=C and C-O stretching, respectively. A strong absorption at 1176 cm^{-1} was attributed for P=N stretching of the cyclotriphosphazene ring. The P-O-C bending can be observed at 977 cm^{-1}. No broad absorption band for the O-H stretching, which confirmed that the insertion of 4-hydroxybenzaldehyde into cyclotriphosphazene core was successful.

The synthesized monosubstituted compound, **5** was used to produce new monosubstituted cyclotriphosphazene based molecules with different substituents (Scheme 4). The IR spectra of compounds **6a, 6b, 7** and **8** showed the same absorption pattern (Figure 2). All compounds showed the absorption bands for C=N, C=C, C-O and C-N stretching at 1600, 1510, 1250 and 1160 cm^{-1}. Absorption band at 1180 cm^{-1} was assigned to P=N stretching while the absorption in the region of 980 to 1070 cm^{-1} was assigned to P-O-C bending. Compounds **6a** and **6b** showed absorptions at 2839 and 2900 cm^{-1}which were assigned for the symmetrical and asymmetrical C-H (sp^3) stretching of the aliphatic chains in the molecules. Compound **7** showed similar absorption band but with weaker intensity, due to the methoxy substituent in the molecule. The absorption band for C-Cl bending of

compound **8** was observed at 842 cm^{-1}. The absence of the aldehydic C-H stretching of the starting material indicated that the condensation reaction was completed.

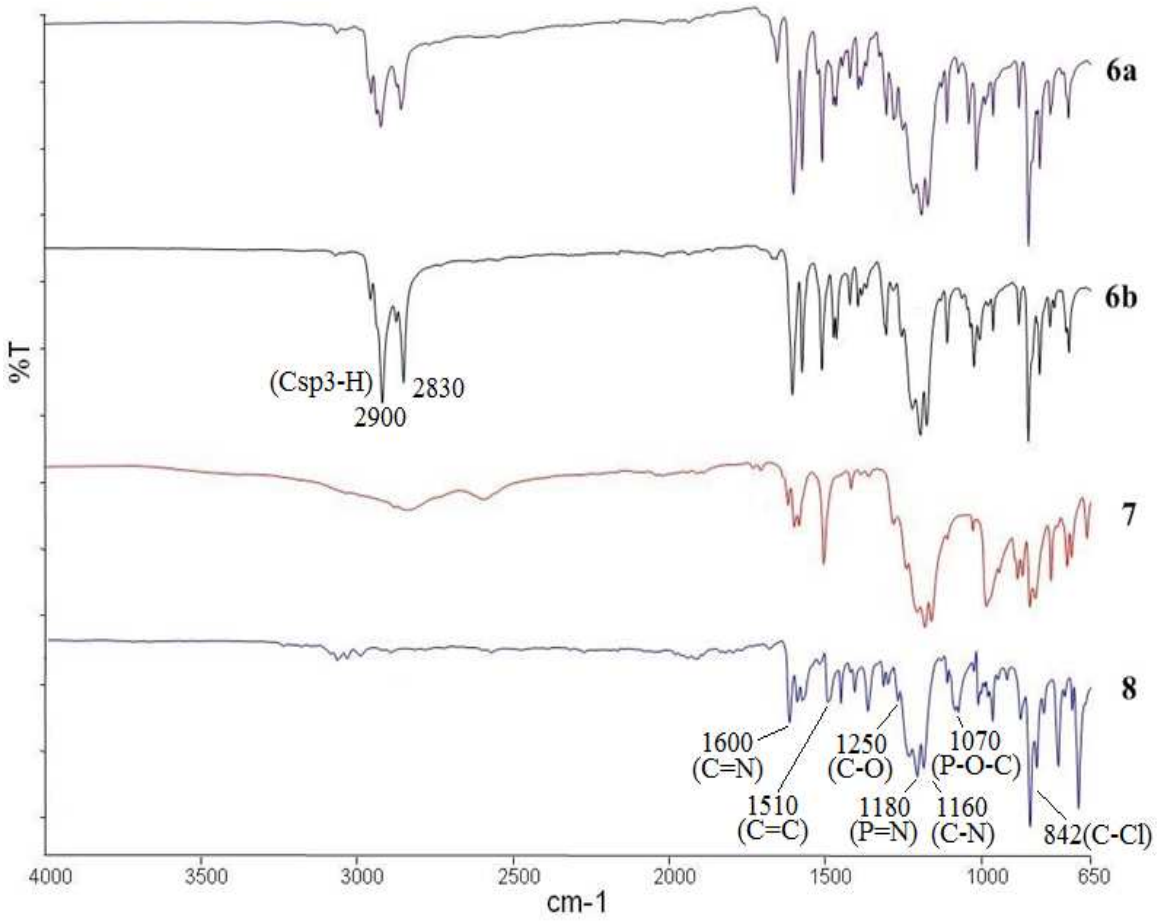


Figure 2. The FT-IR overlay spectra for compounds **6a**, **6b**, **7** and **8**

^{1}H and ^{13}C NMR spectral discussion

The ^{1}H NMR of intermediates **1a** and **1b** revealed the same pattern of signals where the aldehydic proton was observed at δ 9.83 and 9.87 ppm, respectively. Two doublets of the aromatic protons resonated at δ 7.00, 7.81 ppm and 7.02, 7.80 ppm, respectively while 15 aliphatic protons resonated in the upfield region from δ 0.83 to 3.95 ppm for **1a** and 25

protons in the region of δ 0.80 to 3.98 ppm for **1b**. The ^{13}C NMR for intermediates **1a** and **1b** showed 12 and 17 carbon signals, respectively.

The ^{1}H NMR of all compounds **2a, 2b, 3** and **4** showed two singlets of the azomethine protons in the most deshielded region. Six doublets for the aromatic protons were observed in the range of δ 6.90 to 7.87 ppm. Besides, compounds **2a** and **2b** showed 15 and 25 aliphatic protons for the heptyl and dodecyl chains in the upfield region, respectively. The detailed ^{13}C NMR data of all compounds were shown in the experimental section. All compounds showed similar patterns with a methyl carbon at δ 55.38 ppm in compound **3**. Compounds **2a** and **2b** showed the presence of 27 and 32 carbon signals, respectively.

^{1}H-NMR spectrum of monosubstituted cyclotriphosphazene benzalehyde, **5** showed the presence of a singlet at δ 9.97 ppm of the carbonyl proton and two doublets of the aromatic protons at δ 7.92 and 7.41 ppm. ^{13}C NMR spectrum (Appendix 7b-ii) showed a signal at the most downfield region (δ 190.49), assigned for the carbonyl carbon. Two quaternary carbons were assigned for P-O-C (δ 153.56) and C=O (δ 134.66) while other aromatic carbons resonated at δ 122.11, 122.15, 131.67 and 131.69 ppm. ^{31}P NMR spectrum (Figure 3) showed two different phosphorus atoms. A triplet at δ 11.71 ppm was assigned to the phosphorus atom attached to 4-hydroxybenzaldehyde, which coupled to other phosphorus in the cyclotriphosphazene ring. Another two phophorus atoms coupled to the substituted phosphorus to give a doublet at δ 22.48 ppm.

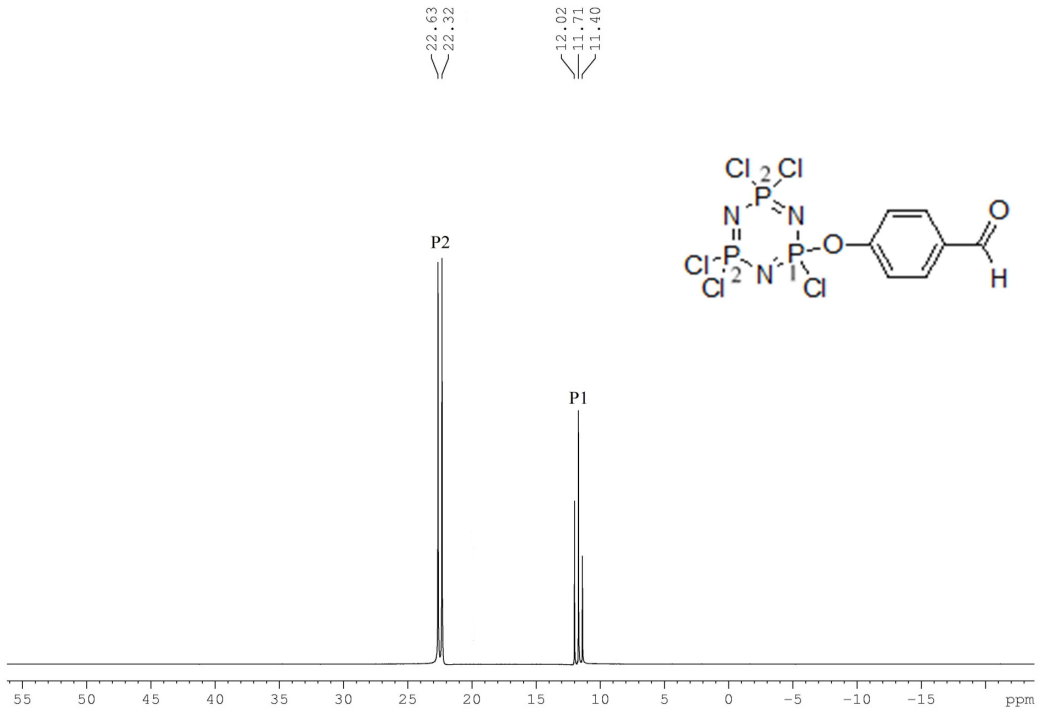


Figure 3. ^{31}P spectrum of monosubstitited cyclotriphosphazene, **5**

The detailed ^{1}H and ^{13}C NMR data were listed in the experimental section. All the compounds showed the similar pattern with the presence of the methoxy proton and carbon for compound **7**. Besides, compounds **6a** and **6b** showed aliphatic protons and carbons for the heptyl and dodecyl chains in the upfield region, respectively. The ^{1}H and ^{13}C NMR of compound **6a** is shown in Figure 4 as an example. The ^{31}P NMR spectra of all compounds showed the same pattern as **5** with two signals since there were two different electron environment of phosphorus in the molecule.

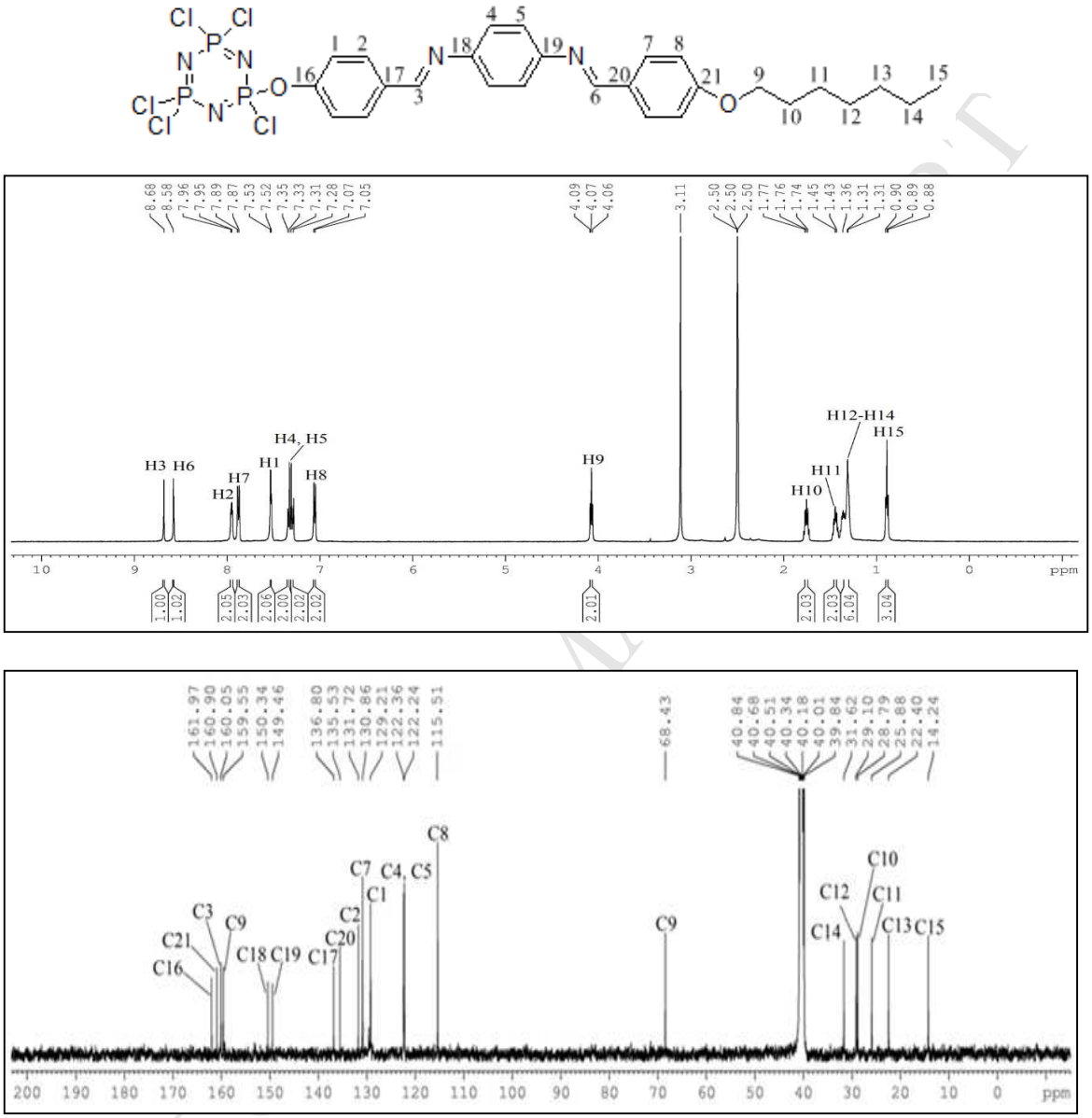
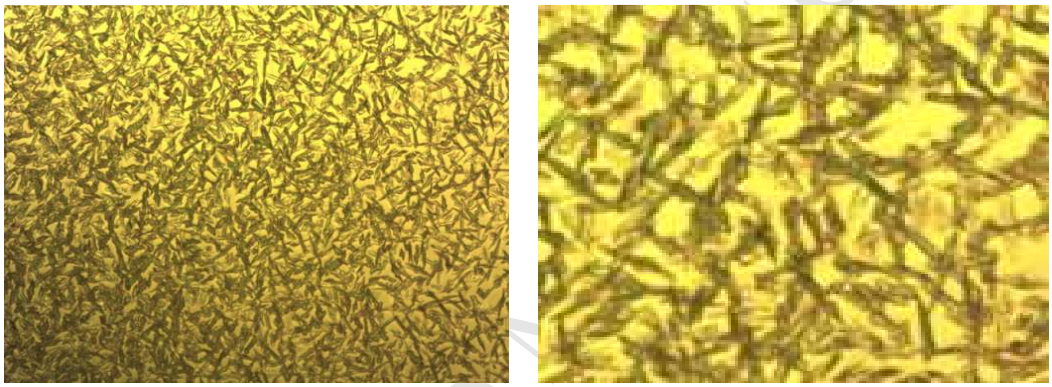


Figure 4. The ^{1}H (500 MHz, DMSO-d_6) and ^{13}C (125 MHz, DMSO-d_6) spectra of compound **6a**

Determination of liquid crystal properties using POM

Determinations of mesophase(s) behaviour for all compounds were done using polarized optical microscope (POM). The heating and cooling rates used for all compounds

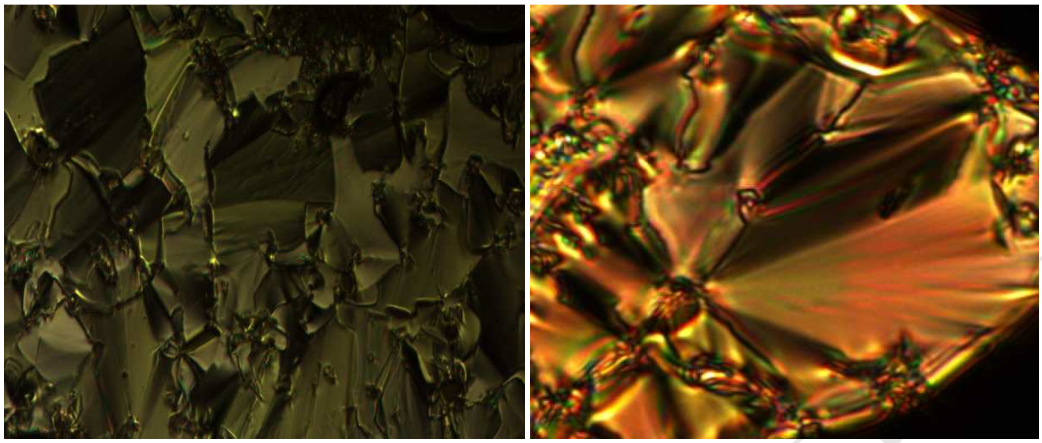
were 5°C/min. Compounds **2a**, **2b**, **6a** and **6b** were found to exhibit liquid crystal mesophase. These compounds can be termed as mesogenic compounds. However, no liquid crystal mesophase was observed for compounds **3**, **4, 7** and **8.** These compounds are non-mesogenic. In the heating cycle, compound **2a** exhibited SmC phase of a broken focal conic fan texture at 118.0ºC before it became the isotropic phase at 145.9ºC. Upon cooling, the SmC phase appeared at 140.3ºC and became the crystal phase at 101.7ºC. The texture of this mesophase is illustrated in Figure 5.



(a) (b)

Figure 5. The POM photographs of broken fan-shaped texture of compound **2a**, observed upon cooling at 139.7ºC. (a) magnification: 20 × 0.40 and (b) magnification: 50 × 0.50

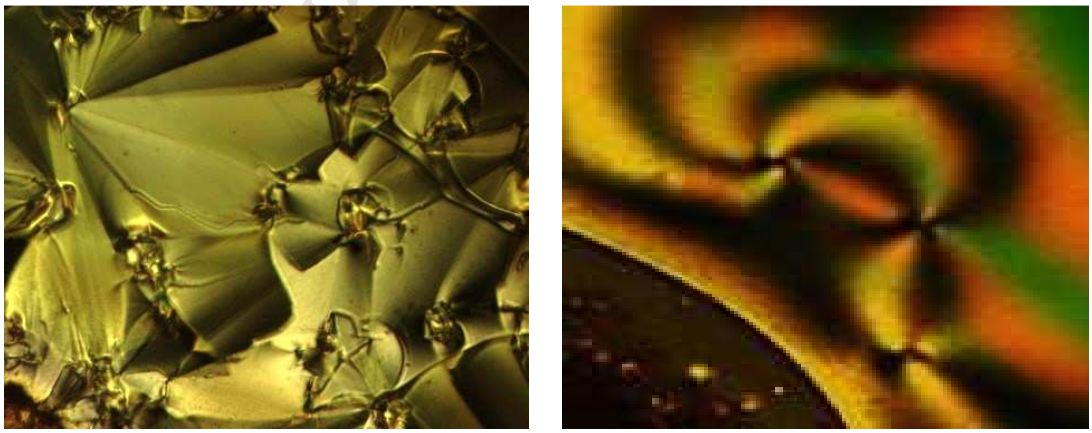
In the heating cycle, compound **2b** showed a SmC phase of a broken focal conic fan texture at 121.5ºC and became isotropic at 128.2ºC. Upon cooling, the isotropic became SmC phase at 122.5ºC before it was transformed into the crystal phase at 109.3ºC. This SmC texture is illustrated in Figure 6.



(a) (b)

Figure 6. The POM photographs of broken fan-shaped texture of compound **2b**, observed upon heating with magnification of 20 × 0.50 at (a) 123.4ºC and (b) 126.3ºC

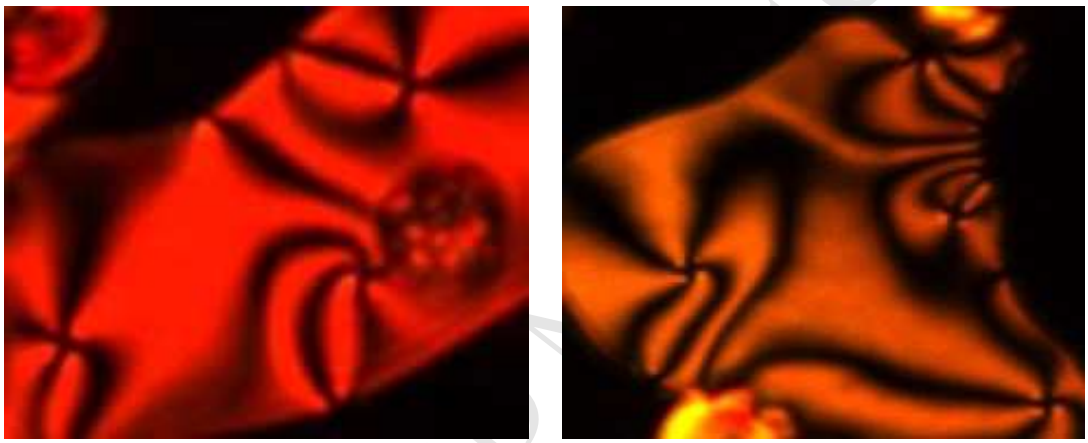
Compound **6a** exhibited two types of liquid crystal phases. In the heating cycle, the crystal phase became the SmC phase of a broken focal conic fan texture at 120.6ºC before it was transformed into the nematic phase of a thread-like texture at 148.5ºC and finally became the isotropic phase at 162.5ºC. Upon cooling, the nematic phase appeared at 172.8ºC, followed by the SmC at 155.6ºC and became the crystal phase at 140.4ºC. The SmC and the nematic textures are illustrated in Figure 7.



(a) (b)

Figure 7. The POM photographs of compound **6a**, observed upon heating with magnification of 20 × 0.50. (a) broken fan-shaped texture of SmC at 121.5ºC and (b) thread-like nematic phase at 149.9ºC

Compound **6b** exhibited the nematic phase of a thread-like texture at 123.9ºC, which then became the isotropic phase at 202.8ºC in the heating cycle. Upon cooling, the nematic phase appeared at 193.1ºC and became the crystal phase at 110.8ºC. The nematic texture is illustrated in Figure 8.



(a) (b)

Figure 8. The POM photographs of a thread-like nematic phase texture of compound **6b**, observed with magnification of 20 × 0.25 at (a) 197.5ºC (heating) and (b) 191.7ºC (cooling)

Determination of thermal transitions using DSC

Compounds **2a**, **2b**, **6a** and **6b** with liquid crystal mesophases were further confirmed using differential scanning calorimetry (DSC) to determine their thermal transitions in the heating and cooling cycles of the compounds. Thermal enthalpy, *ΔH (kJ/mol)* of each transition was calculated and summarized in Table 1 and 2.

Table 1: DSC thermal transitions of compounds **2a**, **2b**, **6a** and **6b** (Heating Cycle)

Compound	**Transition temperature (ºC)** ***Enthalpy, ΔH (kJ/mol)***						
	Cr		**SmC**		**N**		**I**
2a	•	116.05 *5.19*	•	145.25 *4.91*	-	-	•
2b	•	121.16 *11.93*	•	127.51 *2.41*	-	-	•
6a	•	119.04 *13.90*	•	146.58 *11.53*	•	161.39 *2.44*	•
6b	•	122.30 *59.89*	-	-	•	201.73 *12.13*	•

Note: **Cr** = Crystal, **SmC** = Smectic C, **N=** Nematic, **I** = Isotropic

Table 2: DSC thermal transitions of compounds **2a**, **2b**, **6a** and **6b** (Cooling Cycle)

Compound	**Transition temperature (ºC)** ***Enthalpy, ΔH (kJ/mol)***						
	I		**N**		**SmC**		**Cr**
2a	•	-	-	140.95 *-4.50*	•	100.27 *-1.54*	•
2b	•	-	-	123.07 *-2.16*	•	109.68 *-11.46*	•
6a	•	174.81 *2.41*	•	156.90 *2.20*	•	141.96 *7.15*	•
6b	•	194.70 *-8.66*	•	-	-	111.53 *-46.04*	•

Note: **Cr** = Crystal, **SmC** = Smectic C, **N=** Nematic, **I** = Isotropic

The DSC data of compounds **2a**, **2b** and **6b** showed two endotherms in the heating and cooling cycles. The thermogram showed the transitions of crystal-SmC-isotropic phase for compounds **2a** and **2b** while compounds **6b** showed the transitions of the crystal-N-isotropic phase were observed. The DSC thermogram of compounds **6a** showed three endotherms in both cycles which attributed to the phase transitions of SmC and nematic. The DSC thermogram of compound **6a** is shown in Figure 9.

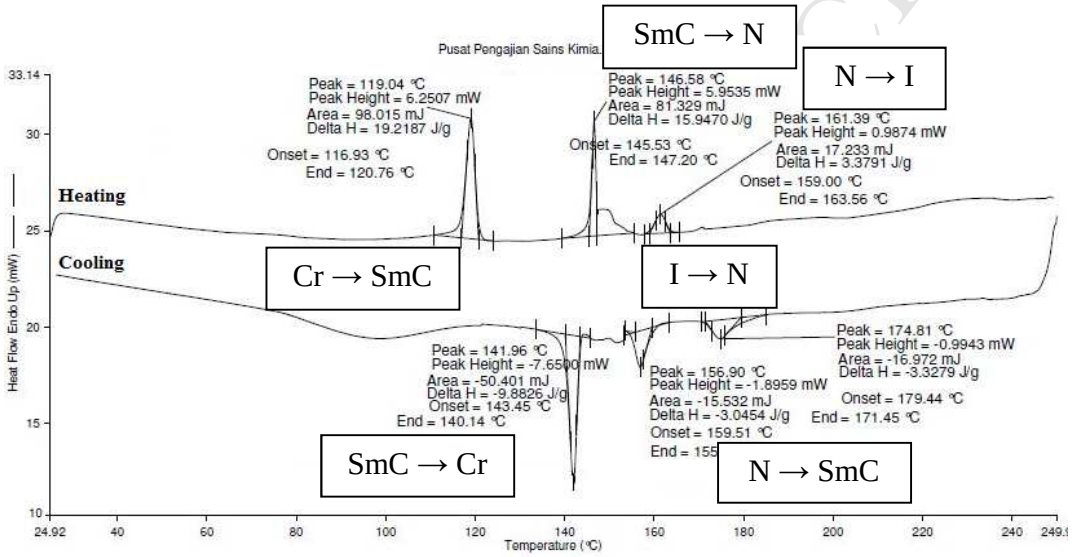


Figure 9. DSC thermogram of compound **6a**.

Structure property relationship

Molecular shape is important in self-assembly of a molecule which gives the impact on the ordering abilities of the mesogenic molecules. In general, a rod-like molecule is composed of flat, rigid cores, linking units and terminal groups of flexible chains [15]. In liquid crystal molecules, linking unit connects one core to another, linking the terminal chain to the core. Schiff base is an example of a linking unit which is very useful in liquid crystal research due to low temperature of phase transitions [16]. Schiff base offers the

possibility of controlling the alignment and orientation of a molecule to generate liquid crystal materials [17]. The linking unit of two Schiff base moieties between the aromatic rings is to increase the length of the molecules, as well as to alter the polarizability and flexibility of the molecules, in which it restricts the freedom of rotation. The extension of the linking unit greatly enhances the nematic-isotropic transition temperature and increases the thermal stability of the nematic order.

The linking unit at the *para* position of the rings is to preserve the linearity of the molecule [18-19]. The interconnected cyclic rings (in this case is benzene) causes the resulting compound to have a linear planar conformation. The nature of the terminal substituents has profound influence on the liquid crystal properties of a compound. It was reported that compounds with shorter alkoxy chains (n=1,3,4) usually able to exhibit nematic phases, while compounds with longer alkoxy chains (n=6,7,8,10,12,14) prone to exhibit SmC phases [20].

The most common core units in liquid crystals are aromatic moieties which are connected through linking unit and they are very useful in providing rigidity to the molecule. It affects the liquid crystal stability and other physical properties, allowing linear configuration. However, decreased ring flexibility has the effect of increasing transition temperature [21-24]. It was reported that conjugation has dramatic effect on the ability of the molecules to self-assemble into liquid crystal mesophases [25].

In this study, compounds (**2a**, **2b**, **6a** and **6b**) with terminal alkyl chains of heptyl and dodecyl showed liquid crystal properties since they possessed stronger attractive forces. The long alkyl chains add flexibility to the rigid core and stabilized the molecular interactions which are needed for the formation of liquid crystal mesophase. This in turn,

increeased the melting temperature, T_m and widen the range of liquid crystal mesophases [26-27]. The increasing alkoxy chain length in a molecule increases the molecular ordering, resulting in more stable mesophases with higher clearing temperatures, T_c, as shown in compounds **6a** and **6b** [20]. There are intermolecular interactions due to the coordinated oxygen atom [28]. The final compounds with flexible alkyl chains attached to a rigid cyclotriphosphazene core showed increased in rigidity. The cyclotriphosphazene ring provides the chemical stability to the structures in the compounds. Thus, it forms more stable mesophases with higher temperatures.

In this work, compounds **4** and **8** with chloro substituent did not exhibit any liquid crystal phases while compounds **3** and **7** with a methoxy substituent also did not exhibit any liquid crystal property. They have low thermal stability to induce liquid crystal mesophase.

CONCLUSION

Intermediates, **1a** and **1b** were synthesized through the alkylation reaction. Further condensation reaction produced a series of Schiff base compounds **2a**, **2b**, **3** and **4**. These compounds were characterized using FT-IR, 1D and 2D NMR spectroscopy and CHN elemental analysis. Reaction of cyclotriphosphazene ring with 4-hydroxybenzaldehyde gave compound **5** which was used for further reaction to yield the final compounds **6a**, **6b**, **7** and **8**. These final compounds were also characterized. Compounds having two Schiff base linking units (**2a**, **2b**, **3** and **4**) were compared with the same compounds attached to cyclotriphosphazene ring (**6a**, **6b**, **7** and **8**). Determination of their liquid crystal mesophase using POM showed that compounds **2a** and **2b** with heptyl and dodecyl chains, respectively, exhibited SmC phases with broken-fan textures. Compound **6a** which is

attached to the cyclotriphosphazene core showed a SmC and nematic phases while compound **6b** showed only a nematic phase. However, compounds **3**, **4**, **7** and **8** were found to be non-mesogenic without liquid crystal mesophase. The thermal transitions for the mesophase transitions were calculated using the DSC thermogram.

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HIGHLIGHTS

- Compounds with two Schiff base linking units and four different substituents was synthesized and characterized.
- The liquid crystal properties of this compounds was determined by polarized optical microscope (POM) and differential scanning calorimeter (DSC).
- Compounds with heptyl and dodecyl substituents showed the liquid crystal properties while compounds with methoxy and chloro substituents were found to be non-mesogenic.