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Synthesis, Structural Elucidation and Mesophase Behaviour of Hexasubstituted Cyclotriphosphazene Molecules with Amide Linking Unit

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Alkylation of 4-acetamidophenol with various alkyl halides gave alkylated derivatives **1a-d** which were further reduced to form amines, **2a-d**. A separate reaction of phosphonitrilic chloride trimer and methyl-4-hydroxybenzoate yielded **3**, hexa-(oxy-4-methyl benzoate)cyclotriphosphazene which was then reacted with ethanol and potassium hydroxide to give **4**, hexa-(oxy-4-benzoic acid)cyclotriphosphazene. This hexasubstituted intermediate **4** was reacted with a series of intermediates **2a-d** to yield the final compounds **5a-d**, hexasubstituted cyclotriphosphazene with amide linking unit. All the structures of the intermediates and final compounds were characterized using Fourier Transform Infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. The liquid crystal properties of all the synthesized compounds were determined using Polarized Optical Microscope (POM). POM observations showed that compounds **5a-d** exhibited liquid crystal properties of smectic A and smectic C phases.

Key words: Liquid crystal; cyclotriphosphazene; amide; smectic A; smectic C

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The discovery of liquid crystal (LC) goes back to 1888 when an Austrian botanist, Friedrich Reinitzer and other researchers observed a cholesteric material having two different melting temperatures upon heating. The material was investigated further by Otto Lehmann using a microscope with high-temperature equipment. This enabled him to observe the polarized light of the newly discovered state of the material which he named as liquid crystal [1]. Later, a German chemist Danel Vorländer expanded Lehmann's work and managed to synthesize a lot of liquid crystal compounds [2].

Liquid crystal is an intermediate phase between liquid and solid, a state of matter that has both the properties of isotropic liquid and solid crystal, which is thermally stable [3]. It can diffuse freely like liquids but somehow it can also retain some physical properties characteristic of a solid crystal. Liquid crystal intermediate state(s) are called mesophase(s), which has orientational order but no positional order [4].

LC can be classified into two categories which are the thermotropic and lyotropic LCs. Thermotropic LC exhibits mesomorphism depending on the temperature while lyotropic LC forms the mesophase(s) based on solvent concentration under certain temperature [5]. The temperature may cause changes on the positional and orientational orders of the molecules which would lead to the changes in the microscopic and macroscopic properties of the liquid crystal [6-8]. The thermotropic LC are divided into two common types which are the calamitic LC (rod-like molecules) and the discotic LC (disc-like molecules). The two most common liquid crystal mesophases are the nematic and smectic phases. Calamitic LC usually exhibits the nematic and smectic phases, while the discotic LC tend to form columnar and nematic phases [9]. The nematic phase occurs at a higher temperature than the smectic phase. The smectic A phase is a linear phase, in which the molecules are perpendicular to the layers whereas the smectic C phase is a tilted phase [10]. The nematic phase exhibit a thread-like texture of four-point brushes while the smectic A and smectic C phases show a focal-conic fan and a broken focal-conic fan texture, respectively.

It is important to choose the suitable core, linking unit or terminal group to obtain a molecule with liquid crystal properties. One of the interesting cores is hexachlorocyclotriphosphazene ($N_3P_3Cl_6$), a ring consisting of alternating phosphorus and nitrogen atoms. This core is an excellent model for the discotic molecules, whereby any side group can replace the chlorine atom attached to the phosphorus

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atoms [11, 12]. Amide is one of the most well-known linking units used in connecting the rigid core groups, which consists of the partial double bond character of the C-N bond. As a result, this compound has high stability and offer the possibility of controlling orientation in the molecules which enables mesophase formation [13]. Meanwhile, the nature of the terminal groups or substituents has the ability to influence the liquid crystal properties of the compound [14]. Substituents are chosen to cover a wide range of steric and electronic nature, which represent the conjugated interaction with the central linking group via the intervening benzene rings [15]. Previous study showed that compound attached to alkoxy side chain demonstrated effect on the mesophase formation [16, 17]. Moriya reported a series of hexasubstituted cyclotriphosphazene derivatives attached to different terminal chains showing a smectic phase [18]. In addition, Joaquín *et al*. (2006) reported the hexasubstituted cyclotriphosphazene derivatives attached to the side arms with an amide linking unit as a dendritic core for the preparation of columnar supermolecular liquid crystals [19].

Hence, this study is focused on the effect of the amide linking unit and alkoxy chain length to the liquid crystal behaviour of the cyclotriphosphaze core system. The aims of this research study are to investigate the structure-properties relationship and the effect of the terminal group, length of the chains and amide linking units to the mesophase behaviour of the compounds.

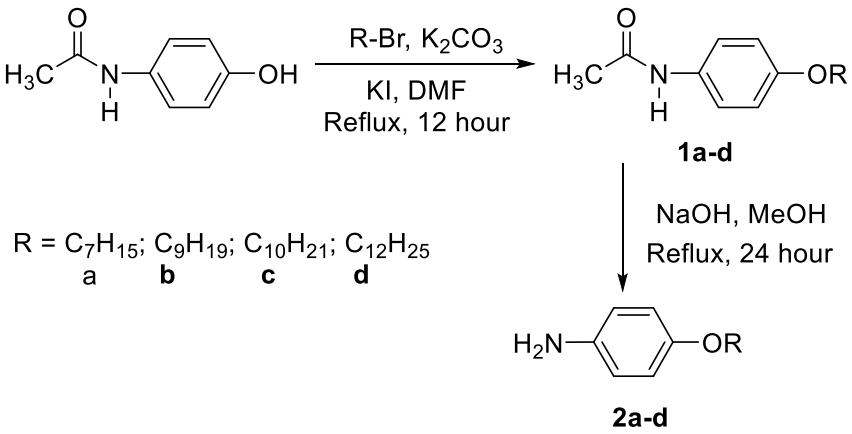
MATERIALS AND METHODS

Chemicals

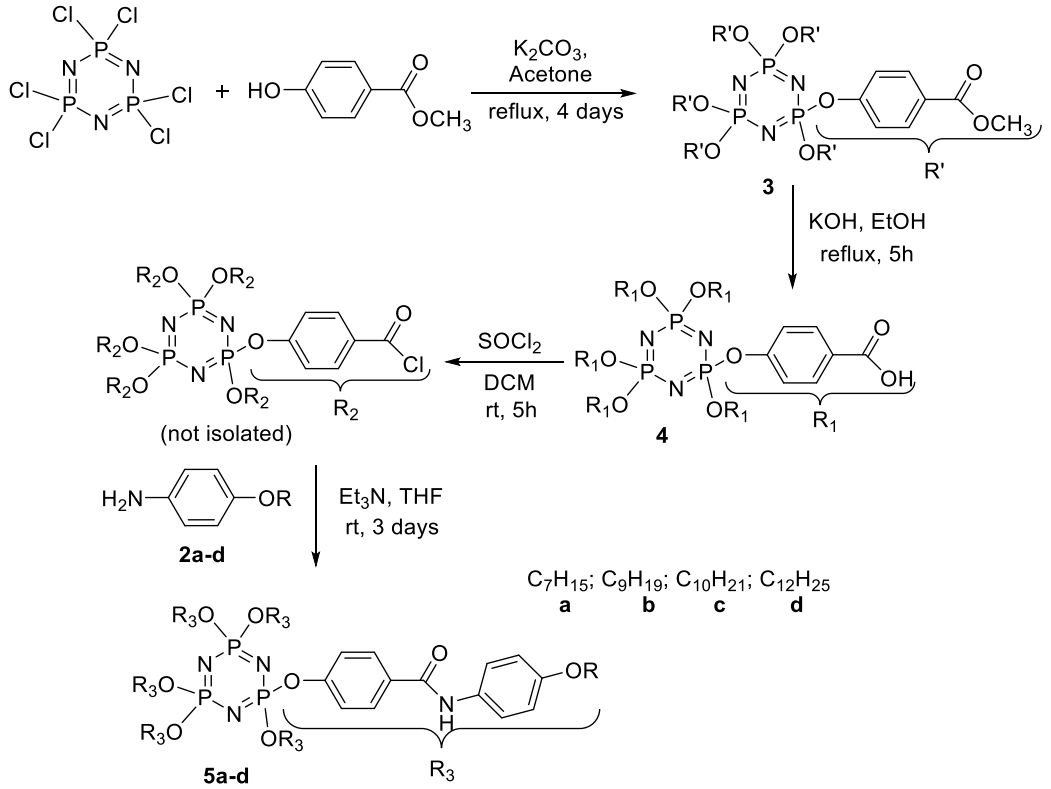
The chemicals and solvents used are methanol, potassium carbonate, sodium hydroxide pellet, potassium hydroxide pellet, ethanol, ethyl acetate, *n*-hexane, acetone, dimethylformamide, dichloromethane tetrahydrofuran, triethylamine, 4-acetamidophenol, methyl-4-hydroxybenzoate, 1-bromoheptane, 1-bromononane, 1-bromodecane, 1-bromododecane and potassium iodide. All the chemicals were purchased from Merck, Qrëc, Sigma-Aldrich and Across, and were used without purification.

Instruments

In this study, thin layer chromatography (TLC) was used used to monitor the progress of the reaction. The functional group of the compound was determined using a FT-IR Perkin Elmer 2000 spectrometer in the range of 600-4000 cm^{-1}. The spectra of ^{1}H, ^{13}C and ^{31}P were obtained using a Bruker 500 MHz Ultrashield^{TM} spectrometer to confirm the structure of the product. Polarized optical microscope (POM) was used to observe the texture of the compounds. The model used was an Olympus system with mesophase bx53 linksys32 temperature control and video capture software. Determination of the liquid crystal mesophase(s) was carried out via observation of a sample during the heating and cooling cycles .



Scheme 1. Synthesis of intermediates **1a-d** [20] and **2a-d** [21].



Scheme 2. Synthesis of hexasubstituted cyclotriphosphazene derivatives, **5a-d** [22-24].

Synthesis Methods

The overall reaction pathways for the formation of the intermediates and hexasubstituted cyclotriphosphazene derivatives are shown in Scheme 1 and Scheme 2, respectively.

N-(4-(heptyloxy)phenyl)acetamide **(1a)**

4-Acetamidophenol (0.10 mol) and 1-bromoheptane (0.10 mol) were dissolved in 60.0 mL DMF separately. Both solutions were mixed in a 250 mL round bottom flask. Potassium carbonate (0.20 mol) and potassium iodide (0.01 mol) were added and the mixture was heated at 80 °C for 12 hours. The reaction progress was monitored using TLC. Upon completion, the mixture was poured into 500 mL of cold water. The precipitate formed was filtered and the crude crystals dried. Recrystallisation from *n*-hexane gave a brown powder. The same method was used to synthesise **1b-d**.

Yield: 87.1%, brown colour crystals.

FTIR analysis (cm^{-1}): 3285 (N-H stretching), 2917 & 2852 (C_{sp3}-H stretching), 1653 (C=O stretching), 1602 & 1507 (C=C stretching), 1472 (amide C-N bending), 1230 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 7.71 (s, 1H), 7.38 (d, *J*=10.0 Hz, 2H), 6.83 (d, *J*=10.0 Hz, 2H), 3.93 (t, *J*=7.5 Hz, 2H), 2.13 (s, 3H), 1.74-1.80 (m, 2H), 1.42-1.48, (m, 2H), 1.32-1.39 (m, 6H), 0.91 (t, *J*=5.0 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 168.56, 156.02, 130.91, 122.01, 114.74, 68.32, 31.78, 29.29, 29.06, 24.20, 22.60 and 14.07.

N-(4-(nonyloxy)phenyl)acetamide **(1b)**

Yield: 84.7%, beige brown colour crystals.

FTIR analysis (cm^{-1}): 3285 (N-H stretching), 2917 & 2852 (C_{sp3}-H stretching), 1653 (C=O stretching), 1602 & 1507 (C=C stretching), 1472 (amide C-N bending), 1230 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 7.56 (s, 1H), 7.35 (d, *J*=10.0 Hz, 2H), 6.79 (d, *J*=10.0 Hz, 2H), 3.88 (t, *J*=5.0 Hz, 2H), 2.10 (s, 3H), 1.71-1.74 (m, 2H), 1.39-1.42, (m, 2H), 1.25-1.32 (m, 10H), 0.86 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 168.46, 156.00, 130.93, 121.83, 114.75, 68.33, 31.87, 31.76 29.53, 29.29, 29.10, 26.16, 24,27, 22.61 and 14.09

N-(4-(decyloxy)phenyl)acetamide **(1c)**

Yield: 83.7%, brown colour crystals.

FTIR analysis (cm^{-1}): 3285 (N-H stretching), 2917 &

2852 (C_{sp3}-H stretching), 1653 (C=O stretching), 1602 & 1507 (C=C stretching), 1472 (amide C-N bending), 1230 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 7.57 (s, 1H), 7.35 (d, *J*=10.0 Hz, 2H), 6.79 (d, *J*=5.0 Hz, 2H), 3.88 (t, *J*=12.5 Hz, 2H), 2.10 (s, 3H), 1.71-1.74 (m, 2H), 1.39-1.42, (m, 2H), 1.25-1.29 (m, 12H), 0.85 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 168.46, 156.00, 130.93, 121.95, 114.74, 68.33, 31.89, 31.82, 29.57, 29.51, 29.31, 29.23, 26.03, 24.26, 22.67 and 14.10.

N-(4-(dodecyloxy)phenyl)acetamide **(1d)**

Yield: 86.1%, brown colour crystals.

FTIR analysis (cm^{-1}): 3285 (N-H stretching), 2917 & 2852 (C_{sp3}-H stretching), 1653 (C=O stretching), 1602 & 1507 (C=C stretching), 1472 (amide C-N bending), 1230 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 7.50 (s, 1H), 7.37 (d, *J*=10.0 Hz, 2H), 6.83 (d, *J*=10.0 Hz, 2H), 3.91 (t, *J*=7.5 Hz, 2H), 2.17 (s, 3H), 1.72-1.78 (m, 2H), 1.26-1.43, (m, 18H), 0.88 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 168.56, 155.95, 131.02, 121.94, 115.09, 68.32, 32.80, 31.91, 29.66, 29.60, 29.46, 29.41, 29.34, 26.03, 25.76, 24.26, 22.68 and 14.10.

4-(Heptyloxy)aniline **(2a)**

A solution of compound **1a** (0.03 mol) in 100 mL methanol was combined with a solution of sodium hydroxide, NaOH (50.00 g) in 60 mL of water and the mixture refluxed for 24 hours. The reaction progress was monitored using TLC. Upon completion, the mixture was poured into 500 mL of cold water. The precipitate formed was filtered and the crude crystals dried. Recrystallisation from methanol gave a brown powder. The same method was used to synthesise **2b-d**.

Yield: 98.6%, brown colour crystals.

FTIR analysis (cm^{-1}): 3400 & 3311 (N-H stretching), 2918 & 2851 (C_{sp3}-H stretching), 1511 (C=C stretching), 1238 (C-O stretching.

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 6.77 (d, *J*=10.0 Hz, 2H), 6.66 (d, *J*=10.0 Hz, 2H), 3.90 (t, *J*=7.5 Hz, 2H), 1.75-1.78 (m, 2H), 1.45-1.48 (m, 2H), 1.31-1.39 (m, 6H), 0.92 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 152.44, 139.68, 116.51, 115.71, 68.75, 31.82, 29.46, 29.11, 26.05, 22.62 and 14.09.

4-(Nonyloxy)aniline **(2b)**

Yield: 92.1%, light brown colour crystals.

FTIR (cm^{-1}): 3400 & 3311 (N-H stretching), 2918 & 2851 (C_{sp3}-H stretching), 1511 (C=C stretching), 1238 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 6.72 (d, *J*=10.0 Hz, 2H), 6.61 (d, *J*=10.0 Hz, 2H), 3.85 (t, *J*=7.5 Hz, 2H), 1.70-1.74 (m, 2H), 1.38-1.44 (m, 2H), 1.26-1.33 (m, 10H), 0.87 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 152.40, 139.70, 116.42, 115.70, 68.75, 31.89, 29.56, 29.45, 29.27, 26.08, 22.68 and 14.11.

4-(Decycloxy)aniline **(2c)**

Yield: 98.3%, dark brown colour crystals.

FTIR analysis (cm^{-1}): 3400 & 3311 (N-H stretching), 2918 & 2851 (C_{sp3}-H stretching), 1511 (C=C stretching), 1238 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 6.76 (d, *J*=10.0 Hz, 2H), 6.66 (d, *J*=10.0 Hz, 2H), 3.90 (t, *J*=7.5 Hz, 2H), 1.73-1.79 (m, 2H), 1.42-1.47 (m, 2H), 1.30-1.37 (m, 12H), 0.91 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 152.40, 139.69, 116.43, 115.70, 68.75, 31.90, 31.83, 29.60, 29.45, 29.23, 26.22, 26.08 22.68 and 14.11.

4-(Dodecyloxy)aniline **(2d)**

Yield: 93.4%, dark brown colour crystals.

FTIR analysis (cm^{-1}): 3400 & 3311 (N-H stretching), 2918 & 2851 (C_{sp3}-H stretching), 1511 (C=C stretching), 1238 (C-O stretching).

^{1}H NMR analysis (500 MHz, $CDCl_3$) δ, ppm: 6.73 (d, *J*=5.0 Hz, 2H), 6.63 (d, *J*=10.0 Hz, 2H), 3.87 (t, *J*=5.0 Hz, 2H), 1.68-1.84 (m, 2H), 1.26-1.44 (m, 18H), 0.88 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, $CDCl_3$) δ, ppm: 152.41, 139.67, 116.43, 115.70, 68.76, 31.92, 29.66, 29.64, 29.60, 29.44, 29.35, 26.07 ,22.69 and 14.11.

Hexa-(oxy-4-benzoate)cyclotriphosphazene **(3)**

Phosphonitrilic chloride trimer (0.02 mol) and methyl-4-hydroxybenzoate (0.12 mol) were dissolved separately in 150 mL acetone. Both solutions were mixed in a 250 mL round bottom flask. Then, potassium carbonate, K_2CO_3 (0.20 mol) was added and the mixture refluxed for 4 days. The reaction progress was monitored using TLC. Upon completion, the reaction was stopped and cooled to

room temperature. The precipitate formed was filtered and washed with cold distilled water. The resulting crude was evaporated to dryness to give a white powder.

Yield: 88.7%, white colour crystals.

FTIR analysis (cm^{-1}): 1692 (C=O stretching), 1602 (C=C stretching), 1275 (benzene C-O stretching), 1158 (acid C-O stretching), 943 (C-H bending).

^{1}H NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 7.85 (d, *J*=5.0 Hz, 2H), 6.99 (d, *J*=10.0 Hz, 2H), 3.92 (s, 3H).

^{13}C NMR analysis (125 MHz, DMSO-d_6) δ, ppm: 165.96, 153.62, 131.33, 1127.38, 120.56 and 52.55.

^{31}P NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 7.55.

Hexa-(oxy-4-carboxy)cyclotriphosphazene **(4)**

Compound **3** (0.02 mol) and potassium hydroxide, KOH (0.13 mol) in 150 mL ethanol were refluxed for 5 hours. The reaction was monitored using TLC. Upon completion, the reaction was stopped and cooled to room temperature. The precipitate formed was filtered and washed with cold distilled water. The crude was dried to give a white powder.

Yield: 90.54%, white colour crystals.

FTIR analysis (cm^{-1}): 3002 (O-H stretching), 1692 (C=O stretching), 1602 (C=C stretching), 1275 (benzene C-O stretching), 1158 (acid C-O stretching), 943 (C-H bending).

^{1}H NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 13.02 (s,1H) 7.84 (d, *J*=5.0 Hz, 2H), 7.01 (d, *J*=10.0 Hz, 2H).

^{13}C NMR analysis (125 MHz, DMSO-d_6) δ, ppm: 166.72, 153.26, 131.73, 128.72 and 121.01.

^{31}P NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 8.00.

4-[4'-(Heptyloxyphenylamide)phenoxy]cyclotriphosphazene **(5a)**

A mixture of compound **4** (0.001 mol) and thionyl chloride, $SOCl_2$ (0.008 mol) in 15 mL dichloromethane, DCM were stirred vigorously at room temperature. The progress of the reaction was monitored using TLC. After 5 hours, a solution of 4-(heptyloxy)aniline, **2a (**0.006 mol) in 10 mL tetrahydrofuran, THF was added dropwise into the mixture and the mixture was stirred for another 10 minutes before a dropwise addition of triethylamine (0.30 g, 0.003 mol). The reaction progress was monitored using TLC. The mixture was then stirred at room temperature for 3 days. Upon completion, the reaction was stopped and the precipitate formed was filtered and washed with THF to give a brown powder. Recrystallization from methanol gave a brown compound. The same method was used to synthesize **5b-d**.

Yield: 71.30%, brown colour compound.

FTIR analysis (cm^{-1}): 3398 (N-H stretching), 2917 & 2850 (Csp^3-H stretching), 1699 (C=O stretching), 1606 (aromatic C=C stretching), 1277 (C-N stretching), 1248 (C-O stretching), 1169 (P=N stretching), 946 (P-O-C stretching).

^{1}H NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 10.28 (s, 1H), 7.84 (d, *J*=10.0 Hz, 2H), 7.31 (d, *J*=10.0 Hz, 2H), 7.02 (d, *J*=5.0 Hz, 2H), 7.00 (d, *J*=5.0 Hz, 2H) 3.96 (t, J=10.0 Hz, 2H), 1.67-1.72 (m, 2H), 1.37-1.42 (m, 2H), 1.26-1.28 (m, 6H), 0.86 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, DMSO-d_6) δ, ppm: 166.21, 156.93, 152.70, 131.22, 128.20, 122.95, 120.46, 115.81, 115.29, 67.80, 31.16, 28.56, 28.34, 25.39, 21.97 and 13.88.

^{31}P NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 7.98.

4-[4'-(Nonyloxyphenylamide)phenoxy]cyclotriphosphazene **(5b)**

Yield: 72.60%, brown colour compound.

FTIR analysis (cm^{-1}): 3398 (N-H stretching), 2917 & 2850 (Csp^3-H stretching), 1699 (C=O stretching), 1606 (aromatic C=C stretching), 1277 (C-N stretching), 1248 (C-O stretching), 1169 (P=N stretching), 946 (P-O-C stretching).

^{1}H NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 10.13 (s, 1H), 7.84 (d, *J*=10.0 Hz, 2H), 7.28 (d, *J*=10.0 Hz, 2H), 7.02 (d, *J*=5.0 Hz, 2H), 6.99 (d, *J*=5.0 Hz, 2H), 3.96 (t, *J*=5.0 Hz, 2H), 1.67-1.73 (m, 2H), 1.37-1.42 (m, 2H), 1.24-1.28 (m, 10H), 0.86 (t, *J*=7.5 Hz, 3H)

^{13}C NMR analysis (125 MHz, DMSO-d_6) δ, ppm: 166.71,158.23, 153.24, 131.72, 128.71, 125.32, 124.38, 120.99 115.78, 68.29, 31.71, 29.39, 29.19, 29.07, 29.02, 25.91, 22.54 and 14.40.

^{31}P NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 7.99.

4-[4'-(Decyloxyphenylamide)phenoxy]cyclotriphosphazene **(5c)**

Yield: 70.09%, brown colour.

FTIR analysis (cm^{-1}): 3398 (N-H stretching), 2917 & 2850 (Csp^3-H stretching), 1699 (C=O stretching), 1606 (aromatic C=C stretching), 1277 (C-N stretching), 1248 (C-O stretching), 1169 (P=N stretching), 946 (P-O-C stretching).

^{1}H NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 10.24 (s, 1H), 7.84 (d, *J*=10.0 Hz, 2H), 7.30 (d, *J*=10.0 Hz, 2H), 7.02 (d, *J*=5.0 Hz, 2H), 6.99 (d, *J*=5.0 Hz, 2H),

3.96 (t, *J*=7.5 Hz, 2H), 1.67-1.71 (m, 2H), 1.38-1.41 (m, 2H), 1.28-1.32 (m, 12H), 0.85 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, DMSO-d_6) δ, ppm: 166.21, 157.99, 152.71, 131.21, 128.21, 124.26, 124.17, 120.48, 115.28, 67.79, 31.22, 28.93, 28.88, 28.68, 28.61, 28.51, 25.41, 22.03 and 13.90.

^{31}P NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 8.00.

4-[4'-(Dodecyloxyphenylamide)phenoxy]cyclotriphosphazene **(5d)**

Yield: 70.09%, brown colour compound.

FTIR analysis (cm^{-1}): 3398 (N-H stretching), 2917 & 2850 (Csp^3-H stretching), 1699 (C=O stretching), 1606 (aromatic C=C stretching), 1277 (C-N stretching), 1248 (C-O stretching), 1169 (P=N stretching), 946 (P-O-C stretching).

^{1}H NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 10.20 (s,1H), 7.83 (d, *J*=10.0 Hz, 2H), 7.31 (d, *J*=10.0 Hz, 2H), 7.02 (d, *J*=5.0 Hz, 2H), 6.99 (d, *J*=5.0 Hz, 2H), 3.96 (t, *J*=7.5 Hz, 2H), 1.66-1.72 (m, 2H), 1.38-1.41 (m, 2H), 1.20-1.36 (m, 16H), 0.85 (t, *J*=7.5 Hz, 3H).

^{13}C NMR analysis (125 MHz, DMSO-d_6) δ, ppm: 166.21, 131.22, 128.21, 124.29, 123.95, 120.50, 115.30, 67.80, 31.22, 28.96, 28.94, 28.91, 28.68, 2863, 28.51, 25.41, 22.03 and 13.89.

^{31}P NMR analysis (500 MHz, DMSO-d_6) δ, ppm: 8.00.

RESULTS AND DISCUSSION

FTIR Spectral Analysis

The IR spectra for the intermediates and final compounds are summarized as compact data in the above section. In the alkylation reaction, intermediates **1a-d** were formed whereby the long alkyl chain were inserted into the starting material, 4-acetamidophenol. The successful alkylation is confirmed by the disappearance of the broad absorption of the O-H stretch at 3100-3300 cm^{-1}. The absorption at 3285 cm^{-1} for the N-H stretching and the bands at 2917 and 2652 cm^{-1} correspond to the C_{sp3}-H stretching. Other absorptions are the bands at 1653 cm^{-1} for C=O stretching, 1602 cm^{-1} for the aromatic C=C stretching, 1472 cm^{-1} for C-N stretching and 1230 cm^{-1} of the C-O stretch. Intermediates **1a-d** were then reduced to form intermediates **2a-d**. The amide group were reduced to the amino group. The disappearance of the carbonyl band at 1653 cm^{-1} for the C=O stretching and the appearance of the two spikes of the N-H stretching at 3400 and 3311 cm^{-1} confirmed the successful reaction. Other absorptions include the bands at 2851 and 2918 cm^{-1} for the C-H (sp^3) stretching, at 1607 cm^{-1} for the aromatic C=C stretching, 1469 cm^{-1} for the N-H bending, 1238 cm^{-1} for the C-N stretching and 1030 cm^{-1} for the C-O stretching.

The substitution reaction of hexachlorocyclotriphosphazene with *p*-hydroxy methyl benzoate formed compound **3** which then underwent hydrolysis to form compound **4**. The IR data shows similar absorption bands for both compounds **3** and **4** except for the appearance of a broad absorption of the O-H group at 3200-3400 cm^{-1} which confirmed the successful reaction. Other absorptions include a band at 1693 cm^{-1} for the C=O stretching, at 1602 cm^{-1} for the C=C stretching and at 1158 cm^{-1} for the C-O stretching. Compound **4** reacted with a series of intermediates **2a-d** to form a series of compounds **5a-d**. The presence of the absorption bands at 3398 and 1699 cm^{-1} for the N-H and C=O stretching, respectively shows that the intermediate **2a-d** have successfully reacted to form the amide linking unit which were attached to the cyclotriphosphazene core. The overlay FTIR spectra of compounds **5a-d** are shown in Figure 1.

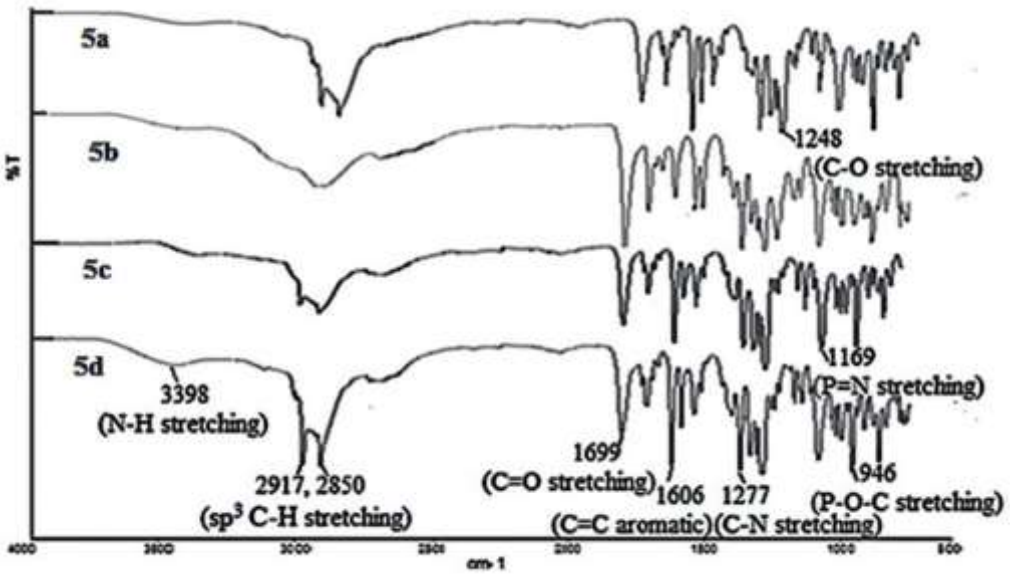


Figure 1. Overlay FTIR spectra of compounds **5a-d**.

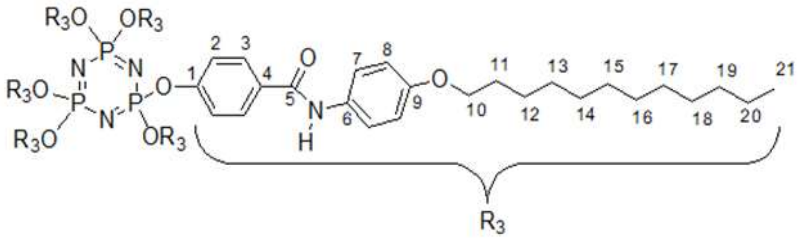
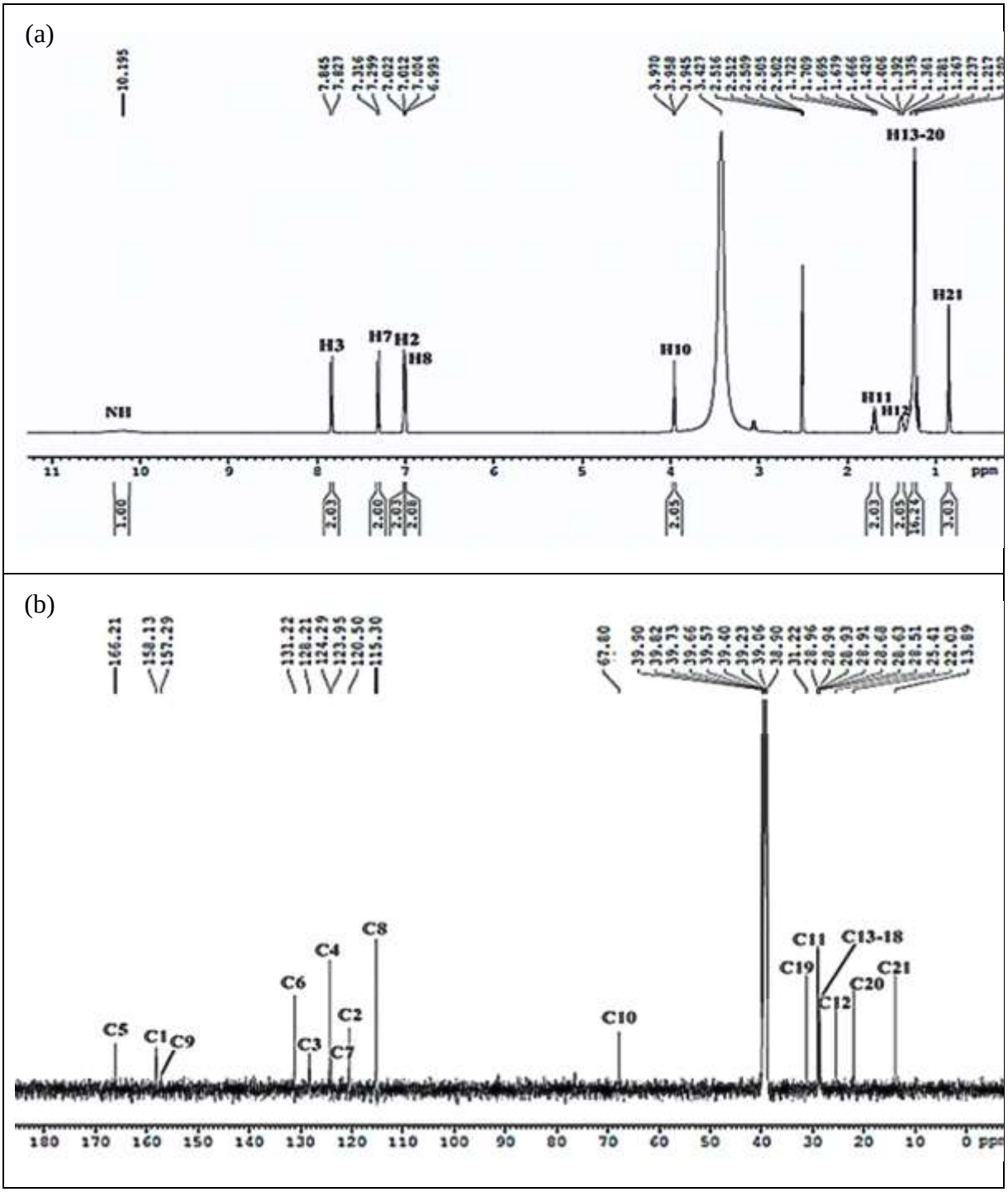


Figure 2. Structure of compound **5d** with complete numbering.



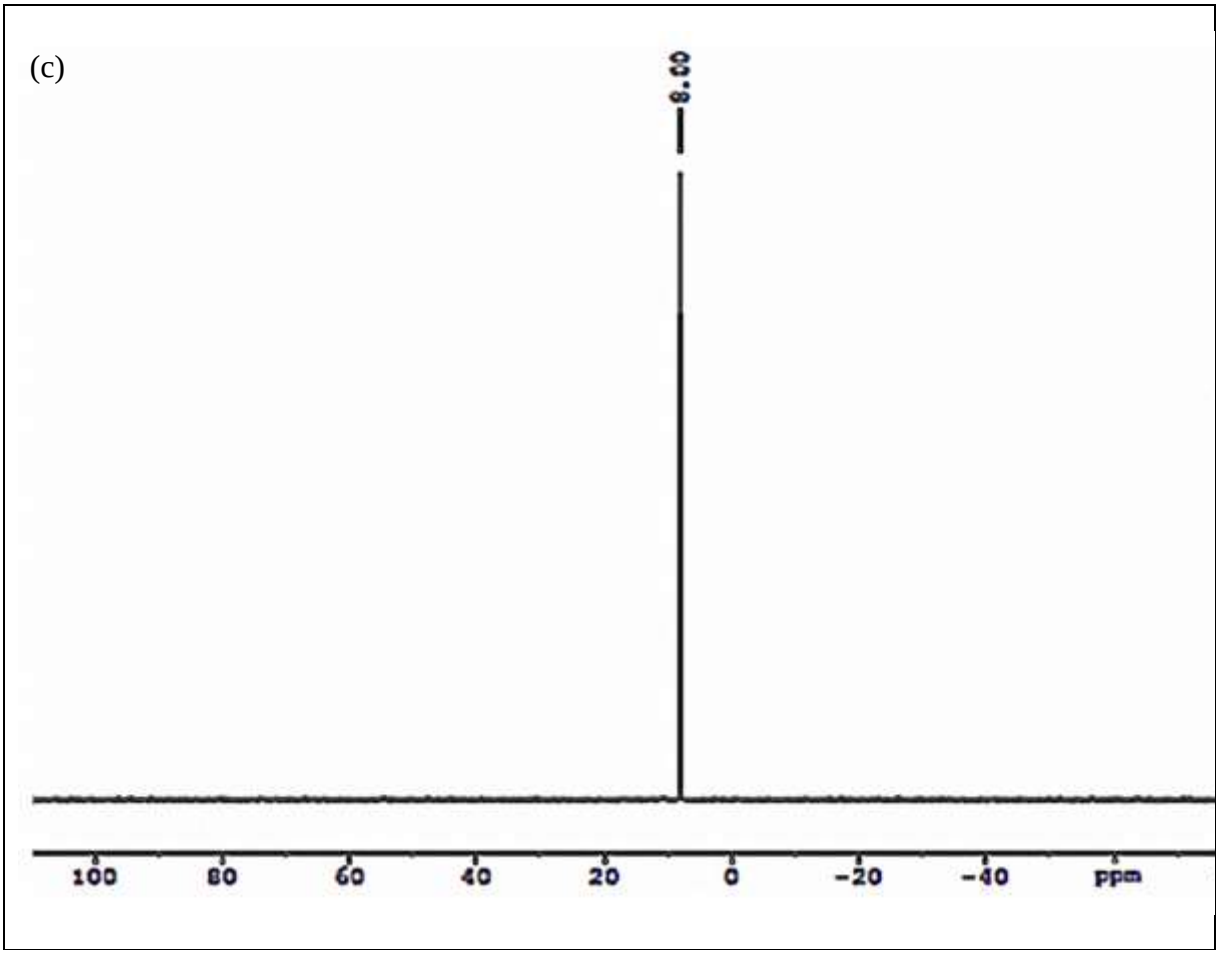


Figure 3. (a) ^{1}H-NMR (500 MHz, DMSO-d_6), (b) ^{13}C-NMR (125 MHz, DMSO-d_6) and (c) ^{31}P-NMR (500 MHz, DMSO-d_6) spectra of compound **5d**.

NMR Spectral Analysis

Intermediate **1d** is used as a representative compound for the NMR spectral discussion. In ^{1}H NMR, the most downfield peak at δ 7.50 ppm is assigned to NH. Two doublets at δ 6.83 and 7.37 ppm are for two different aromatic protons while the terminal nonyl chain shows the most downfield triplet at δ 3.91 ppm, 20 protons as multiplets between δ 1.26-1.78 ppm and the most upfield triplet at δ 0.88 ppm. A singlet at δ 2.17 ppm is for the methyl protons. From the ^{13}C NMR for **1d**, the most downfield peak is the carbonyl carbon for the amide which resonated at δ 168.56 ppm, the aromatic carbons resonated in the region of δ 115.09 to 155.95 ppm and the aliphatic chains carbons in the region of δ 14.10 to 68.32 ppm.

The ^{1}H NMR spectrum representative of intermediate **2d** showed two doublets at δ 6.63 and 6.73 ppm which are attributed to two different aromatic protons, while the terminal nonyl chain shows the most downfield peak at δ 3.87 ppm, 20 protons as multiplets between δ 1.26-1.76 ppm and the most upfield triplet at δ 0.88 ppm. From the ^{13}C NMR for **2d**, the aromatic carbons resonated in the region of δ 115.709 to 152.41 ppmwhile the aliphatic chain carbons resonated in the region of δ 14.11 to 68.76 ppm. The disappearance of the carbonyl and methyl carbon signal at δ 168.56 and 2.17 ppm respectively indicated that the reduction reaction was successful.

Intermediate **3** was a hexasubstituted cyclotriphosphazene attached to a *p*-methyl benzoate. ^{1}H NMR spectrum shows two aromatic protons at δ 6.99 and 7.85 ppm and a singlet for a methyl proton at δ 3.92 ppm. ^{13}C NMR spectrum shows a carbonyl ester carbon at δ 165.96 ppm, four aromatic carbons in the region of δ 120.56-153.62 ppm and a methyl carbon at δ 52.55 ppm. ^{31}P NMR spectrum confirms the successful substitution reaction of all the six Cl atoms. ^{31}P NMR spectrum of intermediate **3** gives only one peak at δ 7.55 ppm.

The ^{1}H NMR spectrum of intermediate **4** shows two doublets for two different aromatic protons at δ 7.84 and 7.01 ppm, while its ^{13}C NMR spectrum shows a carboxyl carbon at δ 166.72 ppm and four signals for four different carbons in the region of δ 121.01-153.26 ppm. The ^{31}P NMR spectrum shows only one peak for phosphorus at δ 7.99 ppm. No methoxy signal was observed in the spectrum as the reaction of **3** with potassium hydroxide are fully utilised.

Compound **5d** was used to represent the structure confirmation of the final compounds. The structure of compound **5d** with complete atomic numbering is shown in Figure 2. The ^{1}H NMR spectrum (Figure 3a) of hexasubstituted cyclotriphosphazene (**5d)** shows a singlet at δ 10.20 ppm attributed to the imine proton. Two benzene rings show four different aromatic protons at δ 6.99, 7.02, 7.31 and 7.83 ppm. The aliphatic nonyl chain shows a triplet at δ 3.96, multiplets at δ 1.38-1.41 and δ 1.20-1.36, and a multiplet at δ 0.85 ppm. The ^{13}C NMR (Figure 3b) shows an imine carbon at δ 166.21 ppm, the aromatic carbons in the regions of δ 166.21-115.30 ppm and the aliphatic carbons in the regions of δ 67.80-13.89 ppm. The ^{31}P NMR spectrum (Figure 3c) shows only one peak for the phosphorus at δ 8.00 ppm.

Determination of Mesophase Behaviour Using POM

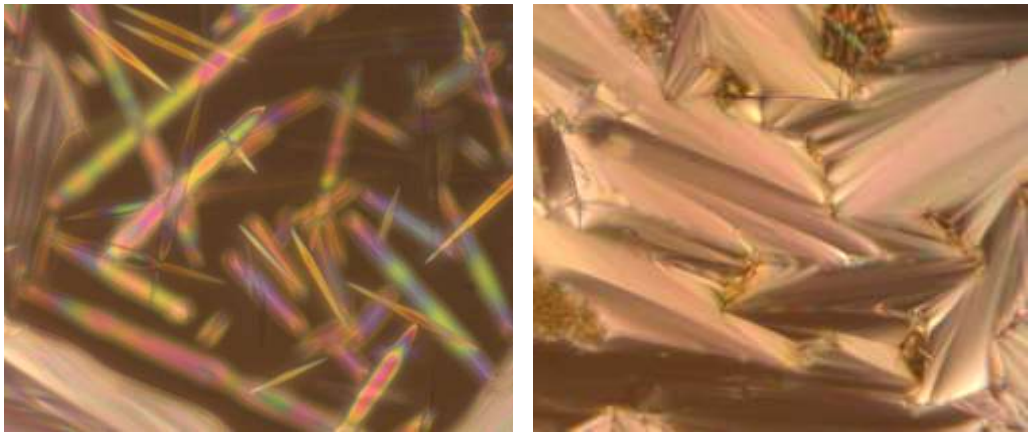
The polarized optical microscope was used to observe the liquid crystal property of all the compounds **5a-d**. The phase transitions and the types of mesophase for these compounds are summarized in Table 1.

All compounds of **5a-d** were analysed in the heating and cooling cycles. All of them showed liquid crystal properties in both cycles which confirmed that all the compounds are enantiotropic. All the textures observed for compounds **5a-d** were captured and shown as POM photographs in Figures 4-7.

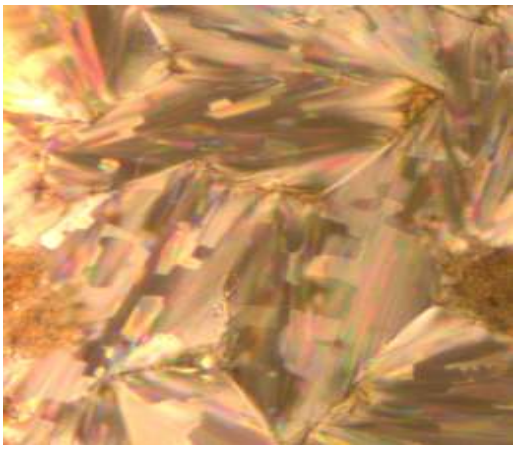
Table 1. POM data for mesophase transitions of compounds **5a-d**.

Compound	Mode	Transition Temperature
5a	Heating	**Cr → SmC → SmA → I** 168.0 ºC 190.7 ºC 220.0 ºC
	Cooling	**I → SmA → SmC → Cr** 223.1 ºC 189.6 ºC 160.0 ºC
5b	Heating	**Cr → SmC → SmA → I** 179.0 ºC 198.8 ºC 232.4 ºC
	Cooling	**I → SmA → SmC → Cr** 230.1 ºC 206.1 ºC 180.0 ºC
5c	Heating	**Cr → SmC → SmA → I** 185.0 ºC 208.5 ºC 236.5 ºC
	Cooling	**I → SmA → SmC → Cr** 233.4 ºC 206.8 ºC 187.6 ºC
5d	Heating	**Cr → SmC → SmA → I** 189.0 ºC 210.7 ºC 239.8 ºC
	Cooling	**I → SmA → SmC → Cr** 237.3 ºC 208.1 ºC 195.0 ºC

Note: **Cr** = Crystal, **SmA** = Smectic A, **SmC** = Smectic C, **I** = Isotropic

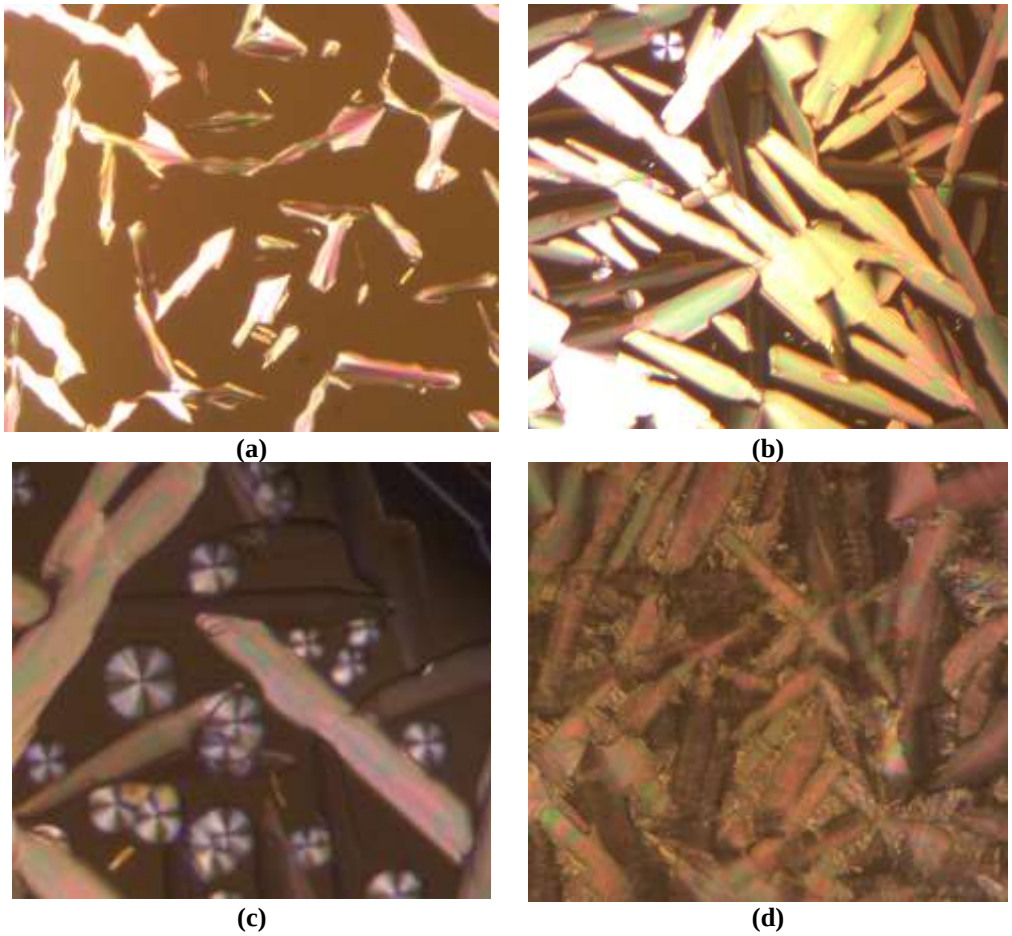


(a) **(b)**



(c)

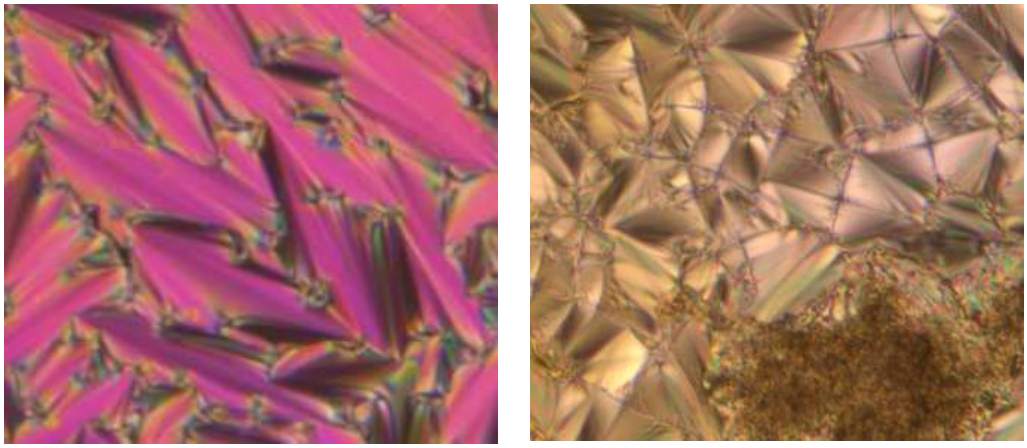
Figure 4. The optical photomicrographs of compound **5a**, (a) batonnet texture at 223.9 ºC, (b) SmA phase at 221.8 ºC and (c) SmC phase at 188.3 ºC, in the cooling cycle with magnification of 10 × 0.40.



(a) **(b)**

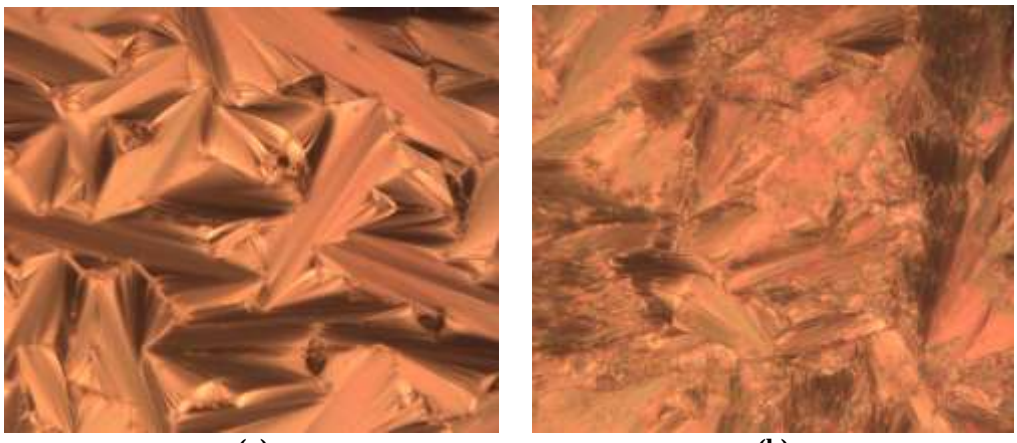
(c) **(d)**

Figure 5. The optical photomicrographs of compound **5b**, (a) batonnet texture at 230.7 ºC, (b) SmA phase at 230.1 ºC, (c) formation of schlieren in the transformation of SmC phase at 206.3 ºC and (d) SmC phase at 204.8 ºC, in the cooling cycle with magnification of 10 × 0.40..



(a) **(b)**

Figure 6. The optical photomicrographs of compound **5c**, (a) smectic A phase at 232.6 ºC and (b) smectic C phase with schlieren at 203.9 ºC, in the cooling cycle with magnification of 10 × 0.40.



(a) **(b)**

Figure 7. The optical photomicrographs of compound **5d**, (a) SmA phase at 235.4 ºC and (b) SmC phase at 207.3 ºC, in the cooling cycle with magnification of 10 × 0.40.

The observations showed that the final compounds **5a-d** were mesogenic. The compounds showed enantiotropic property with a SmA and SmC phase upon the heating and cooling cycle. By increasing the chain length of the molecule, the additional carbon would increase the transition temperature of the compound [25, 26]. Chemical crosslinking would also cause the transition temperature to be increased [27]. Thus, as the chain length of the compound is increased from C_7 to C_{12}, the transition temperature would also be increased as well. The planarity is strengthened by a linkage group. The nature of the partial double bond in the amide linking unit resulted in higher transition and clearing temperatures of the mesogens [13]. Previous study had shown that the incorporation of an amide with an azo linking unit would reduce the broadening effect of the rigid core in the cyclotriphosphazene system, thus causing the molecules to be able to move freely within a layer [22]. This arrangement would give rise to high Van der Waals interactions and intertwining can possibly occur between the alkoxy chains and the amide linking unit [14]. In addition, the presence of the partial C-N bond would reduce the coplanarity which would cause the molecules to be aligned in a lamellar arrangement in the smectic layer [28]. As a result, only SmA and SmC behaviours were observed in this series. The polarisability of the molecules was also increased with an increase in the alkoxy chain length of the compounds [29].

CONCLUSION

A series of rod-like molecules, **1a-d**, **2a-d** and disc-like molecules, **3**, **4** and **5a-d** have been successfully synthesized and characterized. The liquid crystal properties of the final products of hexa-substituted cyclotriphosphazene with an amide linking unit in the side arms, **5a-d**, attached to different terminal chain lengths were determined using polarized optical microscopy. All final compounds showed liquid crystal properties. All compounds have smectic C and smectic A phases. With the increasing lengths of alkyl chain in compounds **5a-d**, the transition temperatures were increased. The additional carbon lengths also increased the transition temperatures of the

compounds. Interestingly, the presence of the partial double bond character of the C-N bond in the amide linking unit led to high rigidities, which resulted in the higher transition and clearing temperatures of the final compounds.

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