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# Liquid Crystalline Cyclotriphosphazenes: Full Substitute Trimeric Derivative with 12-carbon-chain Mesogen Moiety

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#### Abstract

Full substituted p-(dodecyloxy)-phenol derivative of cyclotriphosphazene (trimer) was synthesized in order to investigate its mesogenic properties. Firstly, p-(dodecyloxy)-phenol (**1**) was synthesized from the reaction of hydroquinone and 1-bromododecane. Hexachlorocyclotriphosphazene (trimer) was reacted in a 1:8 molar ratio in tetrahydrofurane (THF) presence of sodium hyride (NaH) as base at room temperature for 24 hours and then under the reflux for a day. Full substituted derivative (**2**) was obtained and its structure was determined by mass analysis, and by FT–IR, <sup>1</sup>H and <sup>31</sup>P {<sup>1</sup>H} NMR spectroscopic techniques. Additionally thermal and mesomorphic behaviours were examined by differential scanning calorimetry (DSC), polarising optical microscopy (POM) and X-ray diffraction (XRD) techniques. By contrast with literature, results showed that compound **2** has liquid crystal behavior.

**Keywords** – Cyclotriphosphazene, Liquid crystal, Differential scanning calorimeter, Polarising optical microscopy, X-ray Diffraction,

# **1** Introduction

Liquid crystals are significant class of compounds and play an important role in the area of technological applications such as displayers, temperature maps, electrical, optical, and switching materials1-11. Cyclotriphosphazenes are considerable starting materials because of having multiarmed rigid ring and their active P-Cl bounds (Figure 1). These features cyclotriphosphazenes of provide an opportunity to replace organic, inorganic and organometallic reactive, by the nucleophilic substitution reaction. Much attention has been focused on several studies of cyclotriphosphazenes because they acquire different physical properties with different side chains or reactives. In addition, cyclotriphosphazenes have been studied in the field of liquid crystals. Some cyclotriphosphazenes derivatives have showed liquid crystallinity [12-31].



Molecular shape is an important factor in the formation of liquid crystal molecules. Generally mesogenic units having one terminal chain on the aromatic ring gives rise to calamitic mesomorphism, whereas the presence of a large number of terminal chains on the aromatic ring causes the molecule to adopt a discotic structure [12-15,30,31]. Calamitic mesomorphism has been reported previously for cyclophosphazene derivatives and this behaviour was explained in terms of a model consisting of mesogenic units arranged approximately perpendicular to the cyclophosphazene ring [16-29]. p-(dodecyloxy)-phenol derivative of cyclotriphosphazene was synthesized and its liquid crystal behaviour was investigated by Moriya et. al. [27] but they didn't found any mesomorphic transition and liquid crystal behaviour in their study. The general aim of this current study was to investigate of liquid crystallinity of compound 2. For this purpose, compound 2 was successfully synthesized according to literature27 and then its liquid crystallinity was examined by POM, DSC and XRD techniques. On the contrary of literature 27, results show that compound 2 has liquid crystal phase transition and it is a liquid crystal molecule.

# 2. Materials and Methods

#### 2.1. Instruments

Elemental analyses were obtained using a Thermo Finnigan Flash EA 1112 series, Italy instrument. Mass analyses were recorded on a Bruker MALDI–TOF (Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight mass, Rheinstetten, Germany) spectrometer for compounds **1** and **2** (using 2,5-dihydroxybenzoic acid Merck, Darmstadt, Germany as matrix). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded with Perkin Elmer Spectrum 100 spectrometer (Perkin Elmer, Waltham, MA, USA). <sup>1</sup>H and <sup>31</sup>P NMR spectra (Varian Inova, West Sussex,

p-dodecyloxy UK) were recorded in CDCl3 solutions on a Varian INOVA 500 MHz spectrometer. Differential Scanning Calorimeter (DSC) measurement of compound 2 was performed on a Mettler Toledo DSC 821 instrument (Mettler Toledo, Columbus, OH, USA) under a protective nitrogen atmosphere from -40 °C to 100 °C at a heating/cooling rate of 10 °Cmin-1. Polarising optical microscopy (POM) was performed using a Leica Wild MPS52 polarizing microscope equipped with Linkam TMS 93 heating and Linkam LNP cooling unit (Leica, Heerbrugg, St. Gallen, Switzerland). Powder X-ray diffraction (XRD) patterns were recorded at room temperature up to resolution of 2<sup>∞</sup> = 2.0–25<sup>°</sup> on a Rigaku X-ray diffractometer D-Max Rint 2200 Series instrument using Cu K $\alpha$  radiation at 40 kV and 40mA.

# 2.2. Chemicals

Trimer was obtained from Aldrich and purified by fractional crystallisation from n-hexane. NaH (Merck,

60% dispersion in mineral oil); prior to use the oil was removed by washing with dry n-hexane followed by decantation. THF, hexane, dichloromethane, dodecanol, 1-bromododecane and hydroquinone were obtained from Merck and used as received. Silica gel (Merck, Kieselgel 60, 70-230 mesh) was used for column chromatography. Reactions were performed under a dry argon atmosphere.

### 2.3. Synthesis

# 2.3.1. Reaction of hydroquinone with 1bromododecane to prepare compound 1

Hydroquinone (5.5 g, 50 mmol) was dissolved in 80 mL of ethanol in a 250 mL three-necked roundbottom flask. 1-bromododecane (6,23 g, 25 mmol) and KOH (2,8 g; 5mmol) added to the stirred solution under argon atmosphere. The reaction was stirred under the reflux for 5 h followed by TLC (Thin Layer Chromatography) on silica gel plates using hekzantetrahydrofuran (4:1) as the mobile phase. The reaction mixture was filtered to remove the salts and any other insoluble material. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using hexane-tetrahydrofuran (4:1) as eluent. pdodecyloxy phenol (1) was isolated.

# 2.3.2. Reaction of trimer with p-dodecyloxy phenol to prepare compound 2

phenol (1) (1.51 g, 5.44 mmol) was dissolved in 20 mL of dry THF in a 100 mL three-necked round-bottom flask. NaH (60% oil suspension, 0.22 g, 5.44 mmol) in 10 mL of dry THF was quickly added to the stirred solution under argon atmosphere. Trimer (0.24 g, 0.68 mmol) dissolved in 10 mL of THF was added dropwise under argon atmosphere. The reaction was stirred for a further 24 h at room temperature and then under the reflux for a day followed by TLC on silica gel plates using hexane-dichloromethane (5:2) as the mobile phase. The reaction mixture was filtered to remove the sodium chloride and any other insoluble material. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography using hexanedichloromethane (5:2) as eluent. The hexakis-[(pdodecyloxy)phenoxy] cyclotriphosphazatrien (2) was isolated.

## 3. Result and Discussion

# 3.1. Synthesis and Characterization

p-(dodecyloxy)-phenol (1) was used as mesogen group and obtained from the reaction of hydroquinone and 1-bromododecane (Scheme 1).



Scheme 1. Reaction of hydroquinone with dodecyl bromide

Trimer was reacted in a 1:8 molar ratio with the sodium derivatives of p-(dodecyloxy)-phenol (1) in THF solution at room temperature. Reactions were monitored by 31P NMR spectroscopy technique and two compounds were seen on spectrum of reaction mixture. Therefore, the reaction was continued under the reflux for 24 hours to obtain full substituted derivative (2) (Scheme 2). The structure of compound 2 was characterised by mass and elemental analyses, and FT–IR, <sup>1</sup>H and <sup>31</sup>P {<sup>1</sup>H} NMR spectra. The element analysis results of compounds 1 and 2 were given in Table 1. Mass spectrum of compound 2 was showed in Figure 2.

N	Empirical Formula	Analytical data (%)						
INU		Calculated			Found			
		C	Н	Ν	C	Н	Ν	
1	$C_{18}H_{30}O_2$	77.7	10.9		77.8	10.9		
2	$C_{108}H_{174}N_3O_{12}P_3$	72.1	9.8	2.3	72.0	9.8	2.3	

Table 1. Analytical data of compounds 1 and 2

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**Scheme 2.** Reaction of hexachlorocyclotriphosphazene with p-(dodecyloxy)phenol



Figure 2. Mass spectrum of compound 2

FT-IR frequencies of various diagnostic bands for the compounds **1** and **2** were given in Table 2. FT-IR spectrum displayed that characteristic C–H aliphatic stretching vibrations in the range of 2851–2923 cm<sup>-1</sup> and aromatic C-C stretching were observed at 1501-1512 cm<sup>-1</sup>. The vibration bands assignable to the stretching of the P–N and P–O for compound **2** were observed at frequency in the range of 1169-1191 cm<sup>-1</sup> and 952 cm<sup>-1</sup>.

**Table 2.** Selected FT-IR vibrations of compounds **1** and **2** (cm<sup>-1</sup>).

	ν	ν	ν	ν	ν
No	(Ar-OH)	(C-H) <sup>1</sup>	(C-C) <sup>1</sup>	(P-N)	(P-O)
1	3423	1605	1512	-	-
	br	m	S		
2	-	1591 m	1501 s	1191 1169 s	952 s

br: broad; s: strong; vs: very strong; m: medium <sup>1</sup> aromatic vibrations

The proton decoupled <sup>31</sup>P NMR spectrum of compound **2** showed only a single peak (A<sub>3</sub> spin systems) at 10.09 ppm because of equal environments of the phosphorus nucleus (Fig.3). The <sup>1</sup>H NMR spectra of compounds **1** and **2** were similar to each other and consistent with the suggested structures; the chemical shifts for CH<sub>2</sub> protons adjacent to O were observed at 3.83-3.90 ppm; the <sup>1</sup>H NMR spectra also showed CH<sub>3</sub> protons at 0.82-0.92 ppm for compounds **1** and **2** respectively. –OH proton of 1 was observed 1.71 ppm. For the aromatic protons, chemical shift values were observed at 6.55-6.82 ppm (Table 3). <sup>1</sup>H NMR spectrum of compound **2** was given as an example in Figure 4.

No	<sup>1</sup> H chemical shift (ppm) <sup>b</sup>				
	-ArH	-OCH2-	<i>H</i> atoms of	-CH <sub>3</sub>	
			other		
			CH <sub>2</sub> groups		
1	6.72-6.65	3.83	1.68-1.19	0.80-0.82	
	(m, 5H)	(t, 2H)	(m, 20H)	(t, 3H)	
2	6.66-6.82	3.88-3.90	1.80-1.29	0.88-0.92	
	(2d, 4H)	(t, 2H)	(m, 20)	(t, 3H)	

Table 3. <sup>1</sup>H NMR parameters for compounds 1 and 2 <sup>b</sup>500 MHz 1H NMR chemical shifts (ppm) in CDCl3 with respect to internal TMS



Figure 4. <sup>1</sup>H NMR spectrum of compound 2

#### 3.2. Mesomorphic Properties

The mesomorphism of compound **2** was studied by DSC, POM and XRD tecniques. The compound gave reproducible DSC curves for heating and cooling over a few cycles and typical thermogram for the third heating and cooling processes was given in Figure 5. Compound **2** containing six p-(dodecyloxy)-phenoxy terminal chains showed two endothermic peaks in the heating cycle of the DSC thermograms at 69.13 °C and at 74.07 °C. In the cooling cycle, **2** has two exothermic peaks which were observed at 53.11 °C and 48.43 °C. (Fig.5). (The first endothermic peak at 69.13 °C belongs to a crystal-liquid crystalline transition, the second endothermic peak at 74.07 °C belongs to a liquid crystalline-izotropic liquid

transition). The corresponding phase transition temperatures and associated enthalpy changes ( $\Delta$ H) of transition were summarized in Table 4.



**Figure 5.** DSC termograms of compound **2** 

**Table 4.** Liquid crystal phase transitions ofcompounds 1 and 2

No	Heating	Cooling		
	(°C)ª [∆H] <sup>b</sup>	(°C)ª [∆H] <sup>b</sup>		
1	54.65 [2.48] for Cr-Lc	74.56 [49.17] for I-Lc		
	81.32 [48.68] for Lc-I	29.27 [2.40] for Lc-Cr		
2	69.13 [23.90] for Cr-Lc	53.11 [55.07] for I-Lc		
	74.07 [109.01]for Lc-I	48.43 [53.85] for Lc-Cr		

Heating and cooling rates: 10°C, heating range: -40-100°C

<sup>a</sup>Thermal transitions detected on the third heating scan (10 °Cmin<sup>-1</sup>). Cr = crystal, LC = liquid crystal, I = isotropic liquid

<sup>b</sup>Enthalpies [ΔH] of transition values in kJmol<sup>-1</sup>

The sample for POM investigation was prepared as a thin film between two glass plates by melting before visual inspection and the POM image for compound 2 was shown in Figure 6. POM investigating of compound 2 supported results of DSC measurements. During the heating process, compound 2 initially appeared as liquid crystal textures under the microscope and the basic texture remained unchanged until the isotropic phase transition. During the cooling process, the same texture occurred again on each side of the film. Although the texture image of 2 was protected until room temperature, below the crystal-liquid crystal transition temperatures, the fluidity of these

materials was lost and a cracked zone took place on the film surfaces by mechanical stress.



**Figure 6.** POM image of compound **2**(magnification 40x)

Images of liquid crystal texture for the compound **2** was focal conic or broken fan-like which were reminiscent of smectic liquid crystals[28,32]. In compound **2**, side chains connected to the P atoms of the trimer ring are arranged three up and three down, perpendicularly to the ring plane (Fig 7). This shape is suitable for smectic arrangement and its possible arrangement was illustrated in Figure 8.



Figure 7. Molecular shape of compound 2



compound 2

The compound was also investigated by powder Xray diffraction (XRD) at room temperature in order to gain more information on the organization of layers. For this purpose, thermal treated film sample was prepared for XRD analysis. The XRD patterns of the compound 2 had a strong-sharp peak in the small angle region (SAXS) at  $2\theta = 2.18^{\circ}$ . This peak indicated that the molecules arranged in regularly spaced layers with the layer distance depended on length of terminal chains as 40.49 Å for compound 2. In addition, the broad diffraction bands observed at  $2\theta$  = 20-25° and in the wide angle region (WAXS) implied the disordered packing of melt hydrophobic alkyl chains in the layer 28,33-38. XRD result supported liquid crystallinity of 2 (Table 5). XRD diffractogram of compound 2 was shown in Figure 9.



Figure 9. XRD diffractogram of compound 2

<b>Tuble 5.</b> And results of compound <b>1</b> and <b>2</b>				
No	$2\theta$ angles	d values		
1	2.12° (s) and ≈ 20-25° (w)	41.64 Å		
2	2.18° (s) and $\approx$ 20-25° (w)	40.49 Å		

**Table 5.** XRD results of compound 1 and 2

### 4. Conclusion

Trimeric compound (p-(dodecyloxy)-phenol derivative of cyclotriphosphazene) (2) was synthesized and fully characterized by standard spectroscopic techniques. Liquid crystallinity of compound (2) was confirmed by POM, DSC and XRD techniques. Information on the organization of layers of the compound was obtained by XRD technique. On the contrary of the literature, it was quite important to note that that compound 2 is liquid crystal and has mesomorphic properties. The three mesogenic chains on both sides of the trimer ring plane give rise to smectic phase of calamitic mesomorphism. As a result, it can be concluded that compound 2 might be a suitable candidates for preparation of new liquid crystalline materials.

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