



# **Molecular Crystals and Liquid Crystals**

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# Novel cyclotriveratrylene columnar liquid crystal with three alkyl chains: The balance between the number and length of alkyl chains for liquid crystalline behavior

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#### ABSTRACT

Series of cyclotriveratrylene (CTV) derivatives with triazole ring and three alkyl groups were prepared by one-pot click condensation in yield of 80–88%. The structures and crown conformations were confirmed by NMR and MS. Their liquid crystalline properties were investigated by DSC, POM and XRD analysis. The studies on mesomorphic properties suggested that the CTV derivatives with pentyl, hexyl or dodecyl groups show no mesophase but the one with octadecyl groups possesses ordered hexagonal columnar mesophase. In comparison with the reported columnar CTV liquid crystals with six alkyl chains at least, the CTV columnar CTV liquid crystal with three alkyl chains was reported for the first time. These results suggested a subtle balance between the number and length of alkyl chains for columnar CTV liquid crystalline behavior. **KEYWORDS** Alkyl; cyclotriveratrylene; mesophase; synthesis

# Introduction

Liquid crystalline materials have been paid much attention and exhibited extensive applications [1–5]. In the past decades, columnar liquid crystals, as one of the important part of liquid crystals, attracted considerable research interests based on their unique properties [6, 7]. This kind of subclass of mesophase shows the strong  $\pi$  - $\pi$  stacking action in column, which is favorable for 1D conduction of charge and/or energy, resulting in potential application in organic light-emitting diodes, organic field-effect transistors and organic photovoltaic cells [8–11]. Usually, columnar liquid crystals were obtained by modifying rigid aromatic cores with 4~12 alkyl chains in high symmetric structures. For instances, the columnar liquid crystals containing the rigid core of triphenylene or hexabenzocoronene derivatives with few alkyl chains were investigated up to now [12–19]. Lately, Percec reported series of perylene columnar liquid crystals with the crown conformations [20–23].

Recently, the calixarene skeleton, in which several aromatic groups were bridged by methylene spacers in cyclic structure, was developed to construct columnar liquid crystal successfully. Some columnar calixarene-based liquid crystals were presented by grafting mesogenic

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Figure 1. Three types of the reported CTV liquid crystals.

units on calixarene sketelon [24-32]. Cyclotriveratrylene (CTV), usually adopting crown conformation with bowl-shape structure, also has been used to prepare the liquid crystalline molecules. The survey of literatures suggested that the reported CTV liquid crystals could be divided into three types as shown in Figure 1. For the type (I), three normal alkyl chains were introduced onto CTV and only the nematic liquid crystal were obtained [33–36]. For the types (II) and (III), 6, 9, 12 or 18 alkyl chains were grafted onto CTV, resulting in nematic or columnar mesophase [37–41]. These literatures suggested that the three aromatic rings were not enough to form the strong  $\pi$ - $\pi$  stacking action for columnar CTV liquid crystals. If the other aromatic groups with multiple alkyl chains were introduced onto CTV, the columnar CTV liquid crystals could be prepared based on the strong  $\pi$ - $\pi$  stacking action of the more aromatic groups in most cases. Moreover, the reported columnar CTV liquid crystals possessed six alkyl chains at least in these literatures. But the columnar CTV liquid crystals with 6-18 alkyl chains were usually prepared by stepwise method with complicated separation. Thus, a arisen question is whether the columnar CTV liquid crystal can be obtained with less alkyl chains such as three alkyl chains, because this kind of CTV derivative could be easily prepared by simple one-pot synthesis. In this article, series of CTV derivatives with three alkyl chains (pentyl, hexyl, dodecyl and octadecyl) based on click chemistry were designed and synthesized in high yields with simple procedure. Moreover, their mesomorphic properties implied that only the CTV derivative with three octadecyl exhibited ordered hexagonal columnar mesophase. These results indicated that a balance between the number and length of alkyl chains for columnar CTV liquid crystalline behavior. The length of alkyl chains could make up for the shortage of numbers of alkyl chains in a certain degree. This study reported firstly the columnar CTV liquid crystal with three alkyl chains, supplying a new strategy to design and synthesis of columnar CTV liquid crystals with less alkyl chains and simple synthetic procedure.

# **Results and discussion**

#### Synthesis and characterization

The synthetic routes for novel columnar CTV liquid crystals were exhibited in Scheme 1. As analyzed above, it is difficult to form columnar CTV liquid crystal for normal CTV derivatives due to the weak  $\pi$ - $\pi$  stacking action of the three aromatic rings in CTV skeleton. In Scheme 1, the click chemistry was applied for the synthesis of target compounds, because of not only the high efficient and concise synthetic procedure of click reaction but also the enhancing  $\pi$ - $\pi$  stacking action based on the three new aromatic triazole ring. In the step of



3: R=C<sub>5</sub>H<sub>11</sub>; 4: R=C<sub>6</sub>H<sub>13</sub>; 5: R=C<sub>12</sub>H<sub>25</sub>; 6: R=C<sub>18</sub>H<sub>37</sub>

Scheme 1. The synthetic routes for CTV derivatives 3, 4, 5 and 6.

preparing CTV skeleton, the simple one-pot method was used to synthesize compound **2** with simple separation in high yield. Also, in order to investigate the influence of alkyl length on mesomorphic property, the pentyl, hexyl, dodecyl and octadecyl groups were introduced onto CTV skeleton. As shown in Scheme 1, compound **1** was prepared conveniently by reacting *o*-methoxyphenol with propargyl bromide in yield of 88%. By further treating compound **1** with paraformaldehyde using BF<sub>3</sub>-Et<sub>2</sub>O as catalyst, compound **2** was obtained in 85% yield after a rapid column chromatography. Then, the target compounds **3–6** was synthesized efficiently by the click reaction of compound **2** with the corresponding alkyl azides. The yields were as high as 80–88%. All new compounds showed only one spot on TLC plate under all kinds of solvents, suggesting they were pure compounds.

The structures of these novel CTV derivatives **3–6** were confirmed by MS and NMR spectra. The strong peaks in their HR-MS spectra at 862.4971, 904.5444, 1156.8223 and 1409.1060 were exactly in accordance with the molecular weight of compounds **3–6**. In their <sup>1</sup>H NMR spectra, the proton signals were well assigned for their structures (see SI). Specially, a pair of doublets for the methylene of CTV skeleton certainly supported the crown conformations for these derivatives, which were favorable for the bowl-shape structures. The slight splits of methyl might be attributed the flexibility of the crown conformation based on the non-rigid methylene bridges. The <sup>13</sup>C NMR spectra also agreed with their structures.

#### **Mesomorphic studies**

The mesomorphic behaviors of compounds **3**, **4** and **5** were firstly studied by differential scanning calorimetry (DSC). The results of DSC detection were shown in Figure 2 and the corresponding thermodynamic parameters were summarized in Table 1. One can see that compounds **3**, **4**, and **5** exhibited one endothermic peak on second heating at  $41.5^{\circ}$ C,  $43.3^{\circ}$ C

Comp.	Phase transition <sup>[a]</sup>	$T(\Delta H)$ Heating scan	T( $\Delta H$ ) Cooling scan
3 4 5 6	Cr-Iso(Iso-Cr) Cr-Iso(Iso-Cr) Cr-Iso(Iso-Cr) Cr-CoI(CoI-Cr) CoI-Iso(Iso-CoI)	41.5(15.3) 43.3(12.8) 48.4(11.4) 22.6(18.9) 63.9(2.4)	40.9(8.5) 41.2(10.9) 46.3(10.1) 18.9(16.3) 54.6(2.1)

Table 1. Transition temperatures (°C) and enthalpies  $(kJ \cdot mol^{-1})$  of compounds 3, 4, 5 and 6.

<sup>[a]</sup>Cr = crystalline, Col = columnar phase, Iso = isotropic



Figure 2. The DSC traces of compounds 3, 4, 5 and 6 on second heating and cooling (scan rate  $10^{\circ}$ C min<sup>-1</sup>).

and 48.4°C, respectively. Upon cooling, they also only showed one exothermic peaks at 40.9°C, 41.2°C and 46.3°C, respectively. These results might suggest the solid state-isotropic phase transition and no mesophase for compounds 3, 4 and 5. However, compound 6 with octadecyl groups displayed the utterly different changes on DSC trace in comparison with compounds 3, 4 and 5. On the second heating, two endothermic peaks were obviously observed at 22.6°C and 63.9°C. Upon cooling, two exothermic peaks appeared at 18.9°C and 54.6°C for compound 6. The broad thermic peaks could be attributed to such long wobbly chains and high viscous morphology for melting. These data implied the phase transition of solid state-mesophase-isotropic phase for compound **6**, which were further supported by the investigation of POM (polarizing optical microscopy) and XRD (X-ray diffraction) analysis. The melting points of compounds 3, 4, 5 and 6 increased orderly with the increase of length of alkyl chains. These DSC traces might be explained by the structures of compounds 3, 4, 5 and 6. Due to six aromatic rings in these novel CTV derivatives, the three alkyl chains (pentyl, hexyl and dodecyl) of compounds 3, 4 and 5 were too short to produce the liquid crystalline property. But the octadecyl groups in compound 6 are long enough to induce the appearance of mesophase. The slight hysteresis for exothermic peak of compound 6 was common super-cooling phenomenon for such highly viscous material. The molecular stacking mode of compound 6 in mesophase was further investigated by POM and XRD as follows.

Furthermore, the phase transition behaviors of compounds **3**, **4**, **5** and **6** were investigated by POM. For compounds **3**, **4** and **5**, the white powder melted gradually at 40–50 °C and the whole view became black slowly. On cooling, the clear liquid transferred to the white solid slowly at the corresponding temperatures of the thermic peaks in DSC curves. No obvious mesophase texture was observed for compounds **3**, **4** and **5**. These phenomena indicated the phase transition of solid state-isotropic phase only for compounds **3**, **4** and **5**. However, for compound **6**, the two kinds of phase transitions on heating and cooling were observed clearly. Upon heating, the solid of compound **6** melted and a cloudy liquid appeared slowly. This kind of cloudy liquid became clear gradually over 60 °C. When cooling from the isotropic phase, the cloudy liquid appeared again for compound **6** and turned more and more bright and colorful with specific texture, which became the solid finally with the decrease of temperature. Figure 3 illustrated the texture of compound **6** at crystalline state and mesophase. One can see that compound **6** was small particle with irregular shape in solid state but exhibited



crystalline state

mesophase

Figure 3. The photos of compound 6 under POM at crystalline state and mesophase on cooling at 40 °C (Zoom in 100 times for big box and 500 times for small box).

uniform and regular texture in mesophase. The dark part in mesophase might indicate the coexistence of isotropic and liquid crystalline state, which could be ascribed to the highly viscous morphology at 40 °C. This observed texture possessed the focal-conic pattern, which was the typical characteristic for columnar liquid crystal. All these POM results were in accordance with the DSC data, suggesting that compounds 3, 4 and 5 have no mesophase and compound **6** with three octadecyl groups exhibited columnar mesomorphic property.

The XRD analysis was employed to investigate the possible molecular packing patterns for the mesophase of compound 6. The XRD trace at 40 °C for the mesophase was illustrated in Figure 4. It can be seen that, although the curve was rough in a certain due to the coexistence of isotropic and liquid crystalline state as described in POM analysis, three reflections at 2.18°, 3.78° and 4.36° were observed obviously for compound 6 in the small-angle region. After calculating by the Bragg's formula  $d = \lambda/(2\sin\theta)$ , the corresponding d-spacings were 40.50, 23.38 and 20.25 Å, which agreed with 1:  $1/\sqrt{3}$ :  $1/\sqrt{4}$  for the [100], [110] and [200] planes of hexagonal columnar mesophase. At the wide-angle regions, the broad halos at  $2\theta = 15 \sim 25^{\circ}$  implied the mean distance of 4.5 Å and the short correlation length of alkyl chains. In addition, a small reflection peak at 20.70° was distinguished, suggesting the distance of 4.28 Å. This value was coincident with the typical intracolumnar distance for  $\pi$ - $\pi$  interaction of ordered hexagonal



Figure 4. XRD trace of compound 6 measured at 40 °C.



Figure 5. The proposed schematic representation of the hexagonal columnar mesophase of compound 6.

columnar liquid crystal. All these XRD data supported the hexagonal columnar liquid crystals for compound 6. On the other hand, as estimated by CPK molecular model, the diameter of compound 6 was 71 Å when assuming the straight linear structure for alkyl chains and bowlshape structure for CTV core. After calculation based on the XRD data, the lattice parameter (a) for mesophase of compound **6** was 46.8 Å, which near 35% less than the diameter of compound 6. These results might suggest that the curly structure for alkyl chains or the possible alkyl interdigitation in the neighboring columns. Thus, the possible molecular stacking model for the hexagonal mesophase of compound 6 was proposed in Figure 5. Combing all the analysis of DSC, POM and XRD analyses, it could be summarized that compounds 3, 4 and 5 with pentyl, hexyl or dodecyl groups exhibited no mesophase, but CTV derivative 6 with three octadecyl groups showed good liquid crystalline behavior with ordered hexagonal mesophase. There results indicated a subtle balance between the number and length of alkyl chains for columnar CTV liquid crystalline behavior. The length of alkyl chains could make up for the numbers of alkyl chains and resulted in the columnar mesophase.

# Conclusion

In conclusion, CTV derivatives with three alkylnyl groups were prepared by one-pot method in 85% yield. Further treating it with alkyl azides, the target CTV derivatives with triazole

rings and three alkyl groups was obtained efficiently by the click reaction in yield of 80–88%. The structures and crown conformations were confirmed by NMR and MS. Their liquid crystalline properties were investigated by DSC, POM and XRD. The results implied that the CTV derivatives with pentyl, hexyl or dodecyl groups possess no mesophase but the one with octadecyl groups exhibited ordered hexagonal columnar mesophase. Unlike the reported columnar CTV liquid crystals with six alkyl chains at least, this article reported the CTV columnar liquid crystal with three alkyl chains for the first time. These results indicated that a subtle balance between the number and length of alkyl chains for columnar CTV liquid crystals with less alkyl chains and the simple synthetic procedure.

# **Experimental**

#### **General methods**

The inorganic and organic reagents chemical reagents were purchased from Aladdin LLC and used directly for reaction. The organic solvents of reaction were purified by standard anhydrous methods before application. TLC analysis was done by pre-coated glass plates. Rapid column chromatography was performed by using silica gel (200–300 mesh) as adsorbent. NMR spectra were obtained on a Bruker-ARX 400 instrument at 26 °C by using tetramethylsilane as internal standard. The MS spectra were performed on Bruker mass spectrometer. The phase transitions were examined by POM (Leica DMRX) with a hot stage (Linkam THMSE 600). Thermal analysis was done on DSC (Thermal Analysis Q100) with a scanning rate of 10°C/min under N<sub>2</sub> atmosphere. The XRD curves were measured on SEIFERT-FPM (XRD7), using Cu K $\alpha$  1.5406Å as the radiation source with 40 kV, 30 mA power.

# Synthesis of compound 1

The mixture of o-methoxyphenol (2.0 g, 16 mmol), propargyl bromide (1.5 mL), and K<sub>2</sub>CO<sub>3</sub> (2.7 g, 20 mmol) was stirred and refluxed in 40 mL of dry MeCN for 10 h. The reaction was monitored by TLC technique. As the starting materials were disappeared, the reaction was cooled to room temperature and then treated with 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. The obtained mixture was filtered and the filtrate was washed by distilled water for three times. The organic layer was concentrated under reduced pressure to afford compound **1** as canary yellow liquid in yield of 88%. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 6.82–7.08 (m, 4H, ArH), 4.74 (s, 2H, OCH<sub>2</sub>C), 3.82 (s, 3H, OCH<sub>3</sub>), 2.48 (s, 1H, C=CH).

# Synthesis of compound 2

Under N<sub>2</sub> atmosphere, compound **1** (16 mmol) and paraformaldehyde (0.5 g, 16 mmol) was added in 40 mL of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 5 min under ice bath, 5 mL of BF<sub>3</sub>-Et<sub>2</sub>O was dropped in the reaction system. The obtained mixture was stirred at room temperature for 48 h. Then the solution was washed by distilled water for two times. The organic layer was separated, concentrated and purified by rapid column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 30: 1). Compound **2** was obtained as white solid in yield of 85%. <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.03 (s, 3H, ArH), 6.86 (s, 3H, ArH), 4.72 (bs, 9H, ArCH<sub>2</sub>Ar and OCH<sub>2</sub>C), 3.83–3.85 (m, 9H, OCH<sub>3</sub>), 3.57 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 2.49 (s, 3H, C≡CH). HR-ESI-MS: m/z calculated for C<sub>33</sub>H<sub>30</sub>O<sub>6</sub>: 545.1934 [MNa]<sup>+</sup>, found 545.1947.

#### Synthesis of compounds 3, 4, 5 and 6

The corresponding alkyl bromide (5 mmol) and NaN<sub>3</sub> was stirred in 15 mL of DMF at 50 °C for 10 h. After cooling, the solution was filtered. Then compound **2** (0.52 g, 1 mmol), CuSO<sub>4</sub>·H<sub>2</sub>O (0.39 g, 1.6 mmol) and sodium ascorbate (0.7 g, 3.6 mmol) were added in the filtrate. The obtained mixture was stirred at 60 °C for 24 h. After reaction, the solution was partitioned by 50 mL of distilled water and 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. Then the organic layer was separated and concentrated. The residue was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>: ethyl acetate = 25: 1). Compound **3**, **4**, **5** and **6** was collected as white powder in yields of 80%, 84%, 86% and 88%, respectively.

Compound 3: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.57 (s, 3H, C = CH), 7.06 (s, 3H, ArH), 6.83 (s, 3H, ArH), 5.28 (m, 6H, OCH<sub>2</sub>), 4.73 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 4.29 (m, 6H, NCH<sub>2</sub>), 3.82–3.86 (m, 9H, Me), 3.52 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 1.80~1.87 (m, 6H, CH<sub>2</sub>), 1.28~1.32 (m, 12H, CH<sub>2</sub>), 0.86 (t, 9H, *J* = 8.0 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 148.15, 146.21, 132.04, 131.62, 125.55, 122.93, 115.82, 113.50, 63.17, 56.16, 50.23, 36.15, 29.62, 28.32, 21.96, 13.58. HR-ESI-MS: m/z calculated for C<sub>48</sub>H<sub>63</sub>N<sub>9</sub>O<sub>6</sub>: 862.4974 [M+H]<sup>+</sup>, found 862.4971.

Compound 4: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.57 (m, 3H, C = CH), 7.06 (s, 3H, ArH), 6.83 (s, 3H, ArH), 5.28 (s, 6H, OCH<sub>2</sub>), 4.73 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 4.34~4.25 (m, 6H, NCH<sub>2</sub>), 3.83–3.86 (m, 9H, OCH<sub>3</sub>), 3.54 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 1.80~1.87 (m, 6H, CH<sub>2</sub>), 1.28~1.32 (bs, 18H, CH<sub>2</sub>), 0.89 (bs, 9H, CH<sub>3</sub>); <sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 148.19, 146.34, 132.72, 131.93, 122.73, 116.13, 115.67, 113.41, 63.43,56.07, 50.41, 36.34, 31.13, 30.15, 25.79, 22.48, 13.78. HR-ESI-MS: m/z calculated for C<sub>51</sub>H<sub>69</sub>N<sub>9</sub>O<sub>6</sub>: 904.5444 [M+H]<sup>+</sup>, found 904.5444.

Compound 5: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.57 (s, 3H, C = CH), 7.06 (s, 6H, ArH), 6.84 (s, 6H, ArH), 5.28 (s, 6H, OCH<sub>2</sub>), 4.72 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 4.31~4.25 (m, 6H, NCH<sub>2</sub>), 3.85–3.89 (m, 9H, OCH<sub>3</sub>), 3.53 (d, 3H, *J* = 12.0 Hz, ArCH<sub>2</sub>Ar), 1.90~1.25 (m, 60H, CH<sub>2</sub>), 0.91~0.87 (t, *J* = 6.0 Hz, 9H, CH<sub>3</sub>).<sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 148.05, 146.33, 1132.77, 131.91, 125.06, 122.78, 115.70, 113.22, 63.30, 56.21, 51.45, 50.36, 36.39, 31.91, 30.19, 29.61, 29.34, 29.16, 28.98, 28.83, 26.71, 26.47, 22.69, 14.13. HR-ESI-MS: m/z calculated for C<sub>69</sub>H<sub>105</sub>N<sub>9</sub>O<sub>6</sub>: 1156.8260 [M+H]<sup>+</sup>, found 1156.8223.

Compound **6**: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.57 (s, 3H, C = CH), 7.06 (s, 6H, ArH), 6.82 (s, 3H, ArH), 5.28 (s, 6H, OCH<sub>2</sub>), 4.72 (d, 3H, *J* = 8.0 Hz, ArCH<sub>2</sub>Ar), 4.30~4.25 (m, 6H, NCH<sub>2</sub>), 3.85–3.90 (s, 9H,OCH<sub>3</sub>), 3.53 (d, 3H, *J* = 8.0 Hz, ArCH<sub>2</sub>Ar), 1.18~1.93 (m, 96H, CH<sub>2</sub>), 0.91~0.88(t, *J* = 8.0 Hz, 9H, CH<sub>3</sub>). <sup>13</sup>C NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm):148.20, 146.40, 132.48, 131.53, 122.95, 122.68, 115.73, 113.40, 63.46, 56.28, 50.37, 36.49, 31.85, 30.22, 29.72, 29.58, 29.38, 29.00, 26.51, 22.71, 14.14. HR-ESI-MS: m/z calculated for C<sub>87</sub>H<sub>141</sub>N<sub>9</sub>O<sub>6</sub>: 1409.1077 [M+H]<sup>+</sup>, found 1409.1060.

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#### **Supporting information**

The experimental procedure and the spectral characterization are given in Supporting Information.

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68 🔄 A. RUAN ET AL.

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