Tetrahedron Letters 56 (2015) 5465-5469

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis and mesomorphic properties of novel columnar liquid crystals based on polytopic gallic ethers with multiple-hydrogen bonding cyanuric cores

Hongyu Guo^a, Xiaoting Fang^a, Fafu Yang^{a,b,*}, Yamin Wu^a

^a College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, PR China
^b Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, PR China

ARTICLE INFO

Article history: Received 23 June 2015 Revised 29 July 2015 Accepted 10 August 2015 Available online 12 August 2015

Keywords: Gallic Cyanuric Synthesis Mesophase Hydrogen bond

ABSTRACT

The gallic–cyanuric monomer **4**, gallic–cyanuric dimer **5**, gallic–cyanuric trimer **6** and gallic–cyanuric tetramer **7** containing multiple hydrogen bond were designed and synthesized in yields of 70–80%. Their symmetric structures were characterized by element analyses, FT-IR, ESI-MS, and NMR spectra. Their hexagonal columnar liquid crystalline phases were confirmed by DSC, POM, and XRD analyses. The scope of mesomorphic temperature of compounds **5**, **6**, and **7** is as wide as 45.7, 70.1, and 134.4 °C, respectively. The more gallic ether units are favorable for excellent mesophase.

© 2015 Elsevier Ltd. All rights reserved.

Columnar liquid crystals (LC) have attracted increasing research interest in recent years based on their 1D charge transport and self-healing properties, which make them unique promising candidates for use in organic photoelectric devices, organic field effect transistors, thin film transistors, organic light emitting diodes, etc.¹⁻⁴ Usually, the columnar LCs were easily obtained by symmetric large conjugated aromatic core with several aliphatic side chains. For instance, the triphenylene, phthalocyanine, and hexabenzocoronene derivatives with three to six aliphatic chains were extensively studied as excellent columnar LCs materials.^{5–10} Lately, gallic ethers or their analogues with three long aliphatic chains on their phenolic groups were seen as good structural units to construct novel columnar LCs by connecting with a large conjugated aromatic core. For examples, Laschat described saddle-shaped tetraphenylenes with peripheral gallic esters displaying columnar mesophases.¹¹ Detert reported the synthesis and mesomorphic properties of some tristriazolotriazine derivatives with 1,2-bissubstituted or 1,2,3-tri-substituted alkoxy side chains on phenyl groups.^{12,13} Our groups also presented novel room-temperature liquid crystals of gallic-perylene-gallic trimers.¹⁴ On the other hand, some research showed that the hydrogen bonding made great influences on the formation of liquid crystals when no large conjugated aromatic structure was introduced as core. Maeda

were not large conjugated aromatic ones, the columnar liquid crystals were observed for these compounds unambiguously due to the intermolecular action of hydrogen bonding of multiple amino groups. The synthetic routes for gallic–cyanuric monomer **4**, gallic–cyanuric dimer **5**, gallic–cyanuric trimer **6**, and gallic–cyanuric tetramer **7** are illustrated in Scheme 1. Firstly, according to the

showed several liquid crystals based on hydrogen bonding

supramolecular assemblies by combination with π -conjugated anion receptors.¹⁵ Saigo presented columnar liquid crystals of

3,4,5-tris(11-acryloyloxyundecyloxy)benzoic acid with 2-amino-

1-propanol based on hydrogen bonding.¹⁶ Shin also exhibited

C₃-symmetric hexa-alkylated liquid crystals with interesting trans-

formation from smectogen to discogen via hydrogen bonding.¹⁷ Moreover, Laschat synthesized wedge-shaped 1,2-diamidoben-

zenes forming columnar mesophases via hydrogen bonding,¹⁸ but

the similar wedge-shaped molecules without hydrogen bonding

Nonetheless, the columnar liquid crystal of symmetric polytopic

gallic derivatives without a large conjugated aromatic core was

not concerned so far. Inspired by these successful cases of colum-

nar liquid crystal based on hydrogen bonding, in this Letter, we

designed and synthesized several symmetric polytopic gallic

ethers with triazine cyanuric cores containing multiple amino

groups, which could produce multiple hydrogen bonding. The

mesomorphic studies showed that although these cyanuric cores

were difficult to show the similar columnar liquid crystals.¹



Fetrahedro





^{*} Corresponding author. Tel./fax: +86 591 83465225. *E-mail address:* yangfafu@fjnu.edu.cn (F. Yang).



Scheme 1. The synthetic routes of title compounds 4, 5, 6, and 7.

literature methods,²⁰ by reacting methyl gallate **1** with bromodecane in K₂CO₃/MeCN, gallic derivative **2** with three long alkyl chains was conveniently prepared in yield of 80%. Then the ammonolysis derivatives **3** was obtained by reacting compound **2** with excess ethylenediamine in yield of 86%. On the other hand, it was well known that the three Cl groups of cyanuric chloride could be selectively substituted by changing the reaction temperatures. Thus, the gallic-cyanuric monomer 4 was easily synthesized by the nucleophilic substitution of gallic amide derivative **3** with cyanuric chloride in Na₂CO₃/acetone system under the temperature of 0–5 °C in yield of 80%. Subsequently, reacting compound 3 with gallic-cyanuric monomer 4 afforded galliccyanuric dimer 5 in same reaction system at 35 °C in yield of 76%. Furthermore, gallic-cyanuric trimer 6 was obtained by condensation of compounds 5 with 3 in NaHCO₃/THF system at 60 °C in yield of 70%. Also, by refluxing gallic-cyanuric dimer 5 with p-phenylene diamine in NaHCO₃/THF system at 60 °C, galliccyanuric tetramer 7 was separated in yield of 72% after column

chromatography. It was worthy of noting that all these polytopic gallic ethers with multiple-azo cyanuric cores **4**, **5**, **6**, and **7** were prepared in simple separating procedures of recrystallization or flash column chromatography in yields of 70–80%.

The structures of all new compounds **4**, **5**, **6**, and **7** were confirmed by element analyses, FT-IR, ESI-MS, and NMR spectra. In their ESI-MS spectra, all of them showed corresponding molecular ion peaks (M^+ , MH^+ or MK^+) at 865.2, 1584.6, 2226.1, and 3127.8 which suggested the condensation of mono-, di-, tri-, and tetrasubstituted gallic-cyanuric derivatives was successfully accomplished as expected. In their ¹H NMR spectra, the corresponding proton signals were well assigned to their structures. Moreover, their ¹³C NMR spectra also exhibited corresponding peaks, for examples the peaks for C=O and OCH₂ at approximately 165 and 74 ppm, respectively. All these characteristic data supported certainly the structures of compounds **4**, **5**, **6**, and **7** in Scheme 1.

The differential scanning calorimetry (DSC) was preliminarily used to investigate the mesomorphic behaviors of compounds **4**,



Figure 1. The DSC traces of compounds **4**, **5**, **6**, and **7** on second heating and cooling (scan rate 10 °C min⁻¹).

Table 1 Transition temperatures (°C) and enthalpies (kJ·mol⁻¹) of compounds 4, 5, 6 and 7

Compd	Phase transition ^a	$T(\Delta H)$ heating scan	$T(\Delta H)$ cooling scan
4	Cr-Iso(Iso-Cr)	26.5(13.64)	25.5(12.48)
5	Cr-Col(Col-Cr)	59.6(6.79)	96.1(9.83)
	Col-Iso(Iso-Col)	52.8(8.62)	98.5(8.33)
6	Cr-Col(Col-Cr)	32.8(7.56)	102.9(7.72)
	Col-Iso(Iso-Col)	28.5(7.31)	100.8(8.28)
7	Cr-Col(Col-Cr)	-10.1(10.88)	123.9(4.86)
	Col-Iso(Iso-Col)	-13.9(4.93)	120.5(9.94)

^a Cr = crystalline, Col = columnar phase, Iso = isotropic.

5, **6** and **7**. The results are shown in Figure 1 and Table 1. One can see that gallic–cyanuric monomer **4** showed only one thermic peak upon cooling (25.5 °C) and second heating (26.5 °C), which might indicate it possesses no mesomorphic property. However, gallic–cyanuric dimer **5**, gallic–cyanuric trimer **6**, and gallic–cyanuric tetramer **7** exhibited two thermic peaks for their cooling and second

heating process. Compound 5 had two endothermic peaks at 59.6 °C and 96.1 °C on second heating, and two exothermic peaks at 52.8 °C and 98.5 °C on cooling. Gallic-cyanuric trimer 6 displayed a melting transition at 32.8 °C and a clearing transition at 102.9 °C upon second heating. Upon cooling an isotropic to mesophase transition at 28.5 °C and a crystallization peak at 100.8 °C were detected. Compound 7 presented two phase transition temperatures at -10.1 °C and 123.9 °C for endothermic peaks on second heating and two exothermic peaks at -13.9 °C and 120.5 °C on cooling. These two thermic peaks indicated that compounds 5, 6, and 7 possess the solid state-mesophase and mesophase-isotropic phase transition on cooling and second heating, which were further confirmed by polarizing optical microscopy (POM). The hysteresis phenomena observed for compounds 6 and 7 might be attributed to super-cooling, which was common for such highly viscous materials. Moreover, after calculation, the scope of mesomorphic temperature of compounds 5, 6, and 7 was as wide as 45.7, 70.1, and 134.4 °C, respectively, indicating that the more gallic ether units resulted in the wider temperature of mesophase. The 134.4 °C for compound 7 was outstanding among the scope of mesophase of various gallic liquid crystals.^{11–14}

Furthermore, based on the DSC results, the mesophase textures of compounds **4**, **5**, **6**, and **7** were studied by POM. For compound **4**, no obvious texture of mesophase was seen both upon heating and cooling. However, compounds **5**, **6**, and **7** exhibited clearly two phase transitions of solid state–mesophase and mesophase–isotropic phase on cooling. The temperatures of phase transition were approximately in agreement with the endothermic (or exothermic) peaks of DSC on heating and cooling. The textures for compounds **4**, **5**, **6**, and **7** at corresponding temperatures on cooling are shown in Figure 2. It can be seen that compound **4** showed no liquid crystal texture but the fan-shape textures for compounds **5**, **6**, and **7** were observed clearly, which were the typical columnar liquid crystals.^{21–28} These columnar liquid crystals were further confirmed by X-ray diffraction (XRD) data.

The mesophase structures of compounds **5**, **6**, and **7** were also established by XRD studies at mesomorphic temperatures of 85 °C. Figure 3 shows the intensity versus 2θ plot for compounds **5**, **6**, and **7**. In the small angle region, two peaks were observed



Figure 2. Mesomorphic textures of compounds 4, 5, 6, and 7 obtained under POM on cooling at 85 °C (×400).



Figure 3. XRD traces of compounds 5, 6, and 7 measured at 85 °C.

obviously at 2.58° (or 2.61°, 2.13°) and 2.98° (or 3.01°, 2.51°) for compounds 5, 6, and 7, respectively. The d-spacing derived from these angles were calculated as 34.2 Å (or 33.8 Å, 41.4 Å) and 29.6 Å (or 29.3 Å, 35.5 Å), which were in agreement with the ratios of $2/\sqrt{3}$, suggesting the hexagonal columnar liquid crystal. Moreover, the broad halos at $2\theta = 16-24^\circ$ were assigned to the average distances of the molten alkyl chains on gallic units. The reflections at 23.5° approximately indicated the spacing of approximately 3.8 Å, which is the typical characteristic of intracolumnar order of columnar liquid crystals with π - π interactions. Thus, all these XRD data supported that compounds 5, 6, and 7 were hexagonal lattice for their mesophases. On the other hand, the CPK molecular model indicated that the diameters of compounds 5, 6, and **7** including the gallic units were 35–44 Å approximately, which was a little bigger than the intercolumn distances of compounds 5, 6, and 7 in XRD analysis. These results might indicate

that the aliphatic chains on gallic units were not in the shape of straightforward spread but in curved formation in mesomorphic phases. Figure 4 exhibits the proposed arrangement for the molecular stacking within the columns of compound 6 as representative one. Combining all the data of DSC, POM, and XRD analyses, it could be deduced that compounds 5, 6, and 7 possess the hexagonal columnar liquid crystalline phases. Comparing the structures of compounds 5, 6, and 7 with the previous columnar gallic liquid crystals with large conjugated aromatic cores,^{11–14} it could be seen that the triazine cyanuric cores of compounds **5**, **6**, and **7** without large conjugated aromatic structures but possessing multiple hydrogen bonding, played crucial roles in liquid crystalline behaviors. The multiple hydrogen bonding reduced the flexibilities of triazine cyanuric structures and enhanced the rigidities like a large conjugated aromatic core. These results were in accordance with the previous reports that the hydrogen bonding was favorable for the formation of columnar liquid crystals.^{18,19} To the best of our knowledge, compounds 5, 6, and 7 were the first examples of column liquid crystals based on symmetric polytopic gallic ethers with multiple-hydrogen bonding cyanuric cores.

In conclusion, by using gallate and cyanuric chloride as starting materials, the gallic-cyanuric monomer 4, gallic-cyanuric dimer 5, gallic-cyanuric trimer 6, and gallic-cyanuric tetramer 7 containing multiple hydrogen bonding cyanuric cores were prepared by the step-by-step synthetic methods in yields of 70-80%. Their structures were confirmed by element analyses, FT-IR, ESI-MS, and NMR spectra. Their mesomorphic behaviors were studied by DSC, POM, and XRD. The results suggested that they had the hexagonal columnar liquid crystalline phases although no large conjugated aromatic cores in compounds 5, 6, and 7. The scope of mesomorphic temperature of compounds 5, 6, and 7 was as wide as 45.7, 70.1, and 134.4 °C, respectively. The more gallic ether units resulted in the wider temperatures of mesophase. The studies on the synthesis and mesomorphic properties of gallic units with other cores including multiple hydrogen bonding, and the influences of hydrogen bonding on mesomorphic properties will be studied further in a following work.



Figure 4. Schematic representations of the columnar molecular arrangements and the intermolecular H-bonding of compound 6.

Acknowledgments

Financial support from the National Natural Science Foundation of China (No. 21406036), Fujian Natural Science Foundation of China (No. 2014J01034), Fujian Province Science and Technology Key Project (2014N0025) and the Program for Innovative Research Team in Science and Technology in Fujian Province University were greatly acknowledged.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.08.018.

References and notes

- Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. Nature 1994, 371, 141–143.
- Pisula, W.; Menon, A.; Stepputat, M.; Lieberwirth, I.; Kolbe, A.; Tracz, A.; Sirringhaus, H.; Pakula, T.; Müllen, K. Adv. Mater. 2005, 17, 684–692.
- Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. Angew. Chem., Int. Ed. 2007, 46, 4832–4887.
- 4. Sergeyev, S.; Pisula, W.; Geerts, Y. H. Chem. Soc. Rev. 2007, 36, 1902–1929.
- 5. Kumar, S. Chemistry of Discotic Liquid Crystals; CRC Press: Boca Raton, 2011.
- 6. Yang, F. F.; Bai, X. Y.; Guo, H. Y.; Li, C. C. Tetrahedron Lett. 2013, 54, 409-412.
- 7. Yang, F. F.; Xu, B. T.; Guo, H. Y.; Xie, J. W. Tetrahedron Lett. 2012, 53, 1598–1602.
- 8. Yang, F. F.; Guo, H. Y.; Xie, J. W.; Lin, J. R. Eur. J. Org. Chem. 2011, 26, 5141–5144.

- 9. Ichihara, M.; Suzuki, A.; Hatsusaka, K.; Ohta, K. *Liq. Cryst.* **2007**, 34, 555–559.
- Lee, C. H.; Kwon, Y. W.; Choi, D. H.; Geerts, Y. H.; Koh, E.; Jin, J. I. Adv. Mater. 2010, 22, 4405–4411.
- Wuckert, E.; Hägele, C.; Giesselmann, F.; Baro, A.; Laschat, S. Beilstein J. Org. Chem. 2009, 5. http://dx.doi.org/10.3762/bjoc.5.57.
- 12. Glang, S.; Rieth, T.; Borchmann, D.; Fortunati, I.; Signorini, R.; Detert, H. *Eur. J.* Org. Chem. 2014, 31, 3116–3126.
- 13. Rieth, T.; Marszalek, T.; Pisula, W.; Detert, H. Chem. Eur. J. 2014, 20, 5000–5006.
 - Meng, L.; Wu, Q. M.; Yang, F. F. New J. Chem. 2015, 39, 72–76.
 Maeda, H.; Naritani, K.; Honsho, Y.; Seki, S. J. Am. Chem. Soc. 2011, 133, 88
 - Maeda, H.; Naritani, K.; Honsho, Y.; Seki, S. J. Am. Chem. Soc. 2011, 133, 8896– 8899.
 - 16. Amano, S.; Ishida, Y.; Saigo, K. Chem. Eur. J. 2007, 13, 5186–5196.
 - 17. Park, S.; Ryu, M.; Shin, T. J.; Cho, B. Soft Matter 2014, 10, 5804–5809.
 - Sander, F.; Tussetschläger, S.; Sauer, S.; Kaller, M.; Axenov, K. V.; Laschat, S. Liq. Cryst. 2012, 40, 303–312.
 - 19. Judele, R.; Laschat, S.; Baro, A.; Nimtz, M. Tetrahedron 2006, 62, 9681–9687.
 - Balagurusamy, V. S.; Ungar, K. G.; Percec, V.; Johansson, G. J. Am. Chem. Soc. 1997, 119, 1539–1543.
 - 21. Wicklein, A.; Lang, A.; Much, M.; Thelakkat, M. J. Am. Chem. Soc. 2009, 131, 14442-14448.
 - Bijak, K.; Janeczek; Grucela-Zajac, H. M.; Schab-Balcerzak, E. Opt. Mater. 2013, 35, 1042–1048.
 - Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. Angew. Chem., Int. Ed. 2007, 46, 4832–4835.
 - Paraschiv, J.; Tomkinson, A.; Giesbers, M.; Sudhölter, E.; Zuilhof, H.; Marcelis, A. Liq. Cryst. 2007, 34, 1029–1038.
 - Zhao, B.; Liu, B.; Png, R. Q.; Zhang, K.; Lim, K. A.; Luo, J.; Shao, J.; Ho, P.; Chi, C.; Wu, J. Chem. Mater. 2010, 22, 435–449.
 - Hong, B. Q.; Yang, F. F.; Guo, H. Y.; Jiao, Z. Y. Tetrahedron Lett. 2014, 55, 252– 255.
 - 27. Yang, F. F.; Xie, J. W.; Guo, H. Y.; Xu, B. T. Liq. Cryst. 2012, 39, 1368–1374.
 - 28. Yang, F. F.; Yuan, J.; LI, C. C.; Guo, H. Y.; Yan, X. Y. Liq. Cryst. 2014, 41, 37–143.