

Acetylene-bridged triazine π -conjugated structures: synthesis and liquid crystalline properties

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Abstract: We report the synthesis and liquid crystalline properties of a new type of tribranched compound built up from triazine as the central core and electron-rich triazine rings as peripheral groups. An equimolar mixture of the star-shaped compound based on the 1,3,5-triazine core with 4-dodecyloxybenzoic acid produced an organic salt exhibiting a columnar mesophase with a dendritic growing texture at low temperatures. The liquid crystalline properties of the triazine-based compound and organic salt were investigated by differential scanning calorimetry and polarizing optical microscopy.

Key words: Triazine, liquid crystals, star-shaped materials, hydrogen bonding

1. Introduction

Liquid crystals (LCs) represent an intriguing state of matter that combines mobility and order at a molecular and supramolecular level [1]. Many examples of LCs can be found in nature. Proteins, tobacco mosaic virus, and soap are some of the naturally occurring liquid crystalline materials. An abundant number of synthetically made LC materials are also reported in the literature [2].

Star-shaped compounds based on the 1,3,5-triazine core with triarmed alkoxy groups on the periphery represent octupolar structures with long enough flexible side chains and possess fascinating nonlinear optical (NLO) properties as they may form columnar phase LCs. Alkoxy chains with sufficient length and numbers at the triazine rings provide liquid crystalline phase Col_{hd} [3,4].

Discotic molecules dominate conventional LCs. Therefore, growing attention is devoted to the synthesis and study of unconventional LCs to discover new LC phases and low-temperature applications [5–9]. Star-shaped LCs with small cores and some extended mesogenic units as LC arms provide molecular structures considered to be discotic LCs. They have flexible spacers and may exhibit nematic LC phases rather than a columnar phase, which is ideal for electrooptical application LC displays [10,11].

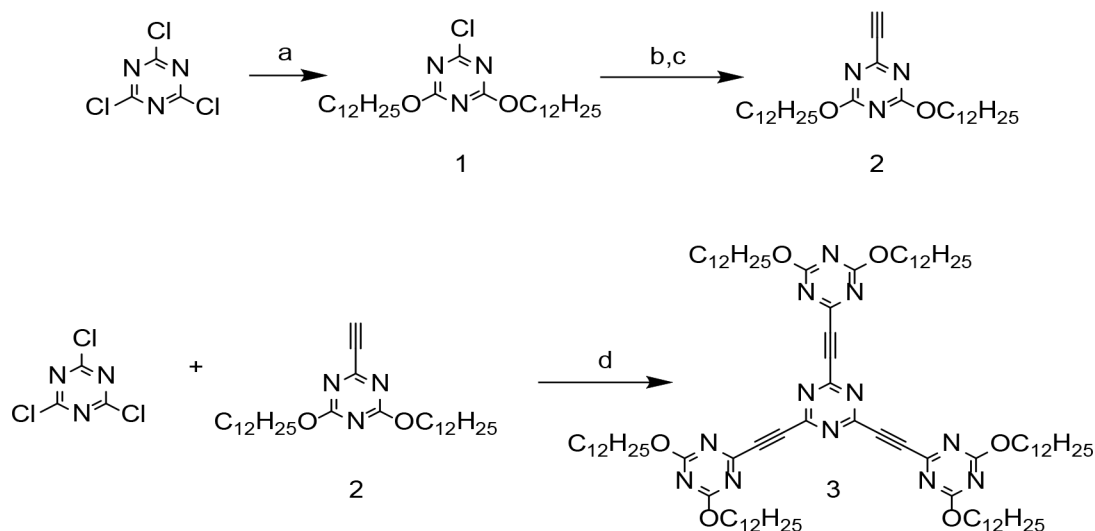
Intensive effort has been devoted to the synthesis of the many kinds of star-shaped LCs to explore their potential applications. A large number of new LCs have been reported based on 1,3,5-triazine in the core with various types of substituents and benzoic acid mesogenic arms [1].

A large number of reports in the literature examine the liquid crystalline properties of charged materials containing anions and cations. Such compounds exhibit low vapor pressure and can replace volatile LCs [12].

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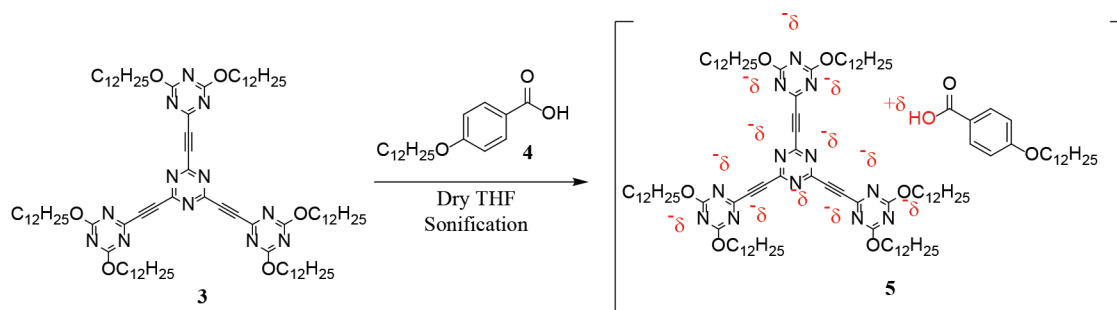
In the present study, we report the preparation and the liquid crystalline properties of a triarmed organic salt utilizing 1,3,5-triazine units in the core and on the periphery, which are substituted with n-dodecyloxy groups as seen in Schemes 1 and 2. The LC was characterized by HRMS, FTIR, ^1H NMR, and ^{13}C NMR analyses. The mesomorphic studies were conducted using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

2. Synthesis



Reactions and conditions: a) 2 eq 1-Dodecanol, 2,2 eq K_2CO_3 , THF, 40-45 °C, 3 h. b) ethynyltrimethylsilane, *n*-BuLi 0 °C 3 h c) f, $\text{CH}_3\text{OH}/\text{THF}$ d) *n*-BuLi -78 °C 2 h then rt 2h.

Scheme 1. Synthesis of 2,4,6-tris((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl)ethynyl)-1,3,5-triazine.



Scheme 2. Synthesis of organic salt.

2.1. Experimental section

2.1.1. 2-Chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (1) [13]

A mixture of 2,4,6-trichloro-1,3,5-triazine (1.9 g, 10.3 mmol), dodecan-1-ol (3.839 g, 20.6 mmol), and K_2CO_3 (2.84 g, 20.6 mmol) in 10 mL of dioxane was stirred at 50 °C for 5 h. The reaction mixture was cooled. The solution was poured into ethyl acetate (20 mL) and the organic layer was separated, washed with water twice

(2 × 10 mL), dried with Na₂SO₄, and the solvent was evaporated under reduced pressure. The material obtained was purified by column chromatography with hexane/ethyl acetate (19:1) as an eluent to give white solid materials (3.5 g, yield: 70%) ¹H NMR (500 MHz, CDCl₃) δ 3.70 (t, *J* = 6.7 Hz, 4H, OCH₂), 1.81–1.51 (m, 4H, CH₂), 1.58–1.20 (m, 36H, CH₂), 0.94 (t, *J* = 6.9 Hz, 6H CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 173.2, 172.2, 68.5, 32.0, 29.7 (2C), 29.6 (2C), 29.4, 29.3, 28.7, 25.9, 22.7, 14.1.

2.1.2. Synthesis of 2,4-bis(dodecyloxy)-6-ethynyl-1,3,5-triazine (2)

Step 1: Trimethylsilylacetylene (0.345 g, 3.51 mmol) was dissolved in dry THF (3 mL). *n*-Butyllithium (2.20 mL, 3.52 mmol, 1.6 M in hexane) was then added dropwise by syringe under argon gas. The reaction mixture was stirred for 1 h under argon gas at 0 °C in an ice bath. Solution of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (1.704 g, 3.52 mmol) in dry THF (8 mL) was then added to the mixture dropwise. The reaction mixture was stirred for 2 h under argon gas at 0 °C in an ice bath. The reaction mixture was allowed to warm up to room temperature. The corresponding compound (2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine) was directly used without isolation and purification in the next step.

Step 2: The mixture of corresponding compound (2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine, 900 mg, 1.65 mmol), K₂CO₃ (684 mg, 4, 95 mmol) in 1:1 MeOH/THF (20 mL) was stirred for 24 h at room temperature. The solution was poured into ethyl acetate (20 mL) and the organic layer was separated, washed with water twice (2 × 10 mL), dried with sodium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude product was subjected to purification by column chromatography with hexane/ethyl acetate (6:1) as an eluent to give yellow liquid materials (2) (700 mg, 42%). ¹H NMR (500 MHz, CDCl₃) δ 3.92 (s, 1H), 3.52 (t, *J* = 6.7 Hz, 4H, OCH₂), 1.50–1.40 (m, 4H, CH₂), 1.33–1.08 (m, 36H, CH₂), 0.77 (t, *J* = 6.8 Hz, 6H, CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 174.1, 173.7, 74.4, 69.2, 63.5, 32.4, 30.1 (2C), 30.0 (2C), 29.8, 29.4, 27.4, 26.2, 23.2, 14.5. HRMS = *m/z* [M+H]⁺ calcd for C₂₉H₅₂N₃O₂: 474.40; found: 474.41.

2.1.3. 2,4,6-Tris((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl)ethynyl)-1,3,5-triazine (3)

n-BuLi (0.65 mL, 1.05 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of 2,4-bis(dodecyloxy)-6-ethynyl-1,3,5-triazine (2) (0.5 g, 1.05 mmol) in THF (8 mL) at –78 °C. The solution was stirred for 1 h, allowed to warm to room temperature, and stirred for another 20 min. The solution was then cooled to –78 °C and a solution of cyanuric chloride (1) (0.055 mg, 0.3 mmol) in THF (1 mL) was added dropwise and the mixture was stirred for 30 min. The mixture was warmed to room temperature and then stirred for an additional 2 h. Water (10 mL) and dichloromethane (10 mL) were added. The aqueous layer was extracted with dichloromethane (2 × 10 mL). The combined organic layers were then washed with brine, dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The resulting crude product was purified by column chromatography (6:1 hexane/ethyl acetate) to obtain the target compound 4 (0.09 g, yield 21%). ¹H NMR (500 MHz, CDCl₃) δ 3.63 (t, *J* = 6.7 Hz, 12H, OCH₂), 1.64–1.50 (m, 12H, CH₂), 1.44–1.22 (m, 108H, CH₂), 0.88 (t, *J* = 7.0 Hz, 18H, CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 173.4, 173.0, 172.4, 92.8, 90.4, 68.8, 32.2, 30.0, 29.9 (2C), 29.8, 29.6 (2C), 28.9, 26.1, 23.0, 14.4. HRMS = *m/z* [M]⁺ calcd for C₉₀H₁₅₀N₁₂O₆: 1495.18; found: 1495.19.

2.1.4. Synthesis of 4-(dodecyloxy) benzoic acid (4-DBA) (4) [14]

A solution of 4-hydroxy benzoic acid (16.43 mmol), 1-bromododecane (11 mL, 46 mmol, 2.8 eq), and KOH (2.58 g, 46 mmol) in ethanol (50 mL) was heated under reflux for 3 days. The resulting material was hydrolyzed with 10% aqueous KOH (25 mL) under refluxing overnight, after which the mixture was cooled to room temperature and acidified with HCl (6 M). The precipitate was filtered, washed with water, and recrystallized from ethanol to give the pure product 4-dodecyloxybenzoic acid as a white solid (4), 4.55 g, 91% yield. ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.93 (d, $J = 6.8$ Hz, 2H, Ar-H), 4.05 (t, $J = 6.4$ Hz, 2H, OCH_2), 1.96–1.68 (m, 2H, CH_2), 1.52–1.27 (m, 18H, CH_2), 0.89 (t, $J = 7.0$ Hz, 3H, CH_3).

2.1.5. Synthesis of organic salt (5)

4-DBA mesogenic unit (4) with a carboxyl group was added to 2,4,6-tris((4,6-bis(dodecyloxy)-1,3,5-triazin-2-yl)ethynyl)-1,3,5-triazine (3) in one to one ratio. Sonication was performed in dry THF for 10 min until a transparent solution was obtained. Then the solvent was removed in a vacuum.

3. Result and discussion

The interaction between the triarmed π -conjugated system and the mesogenic carboxyl group was mainly studied by FTIR. The carboxylic peak at 1680 cm^{-1} in 4-(dodecyloxy) benzoic acid shifted to 1520 cm^{-1} in the salt material 5. However, the C=N peaks were observed in both compound 3 and organic salt at 1505 as seen in Figure 1 [15].

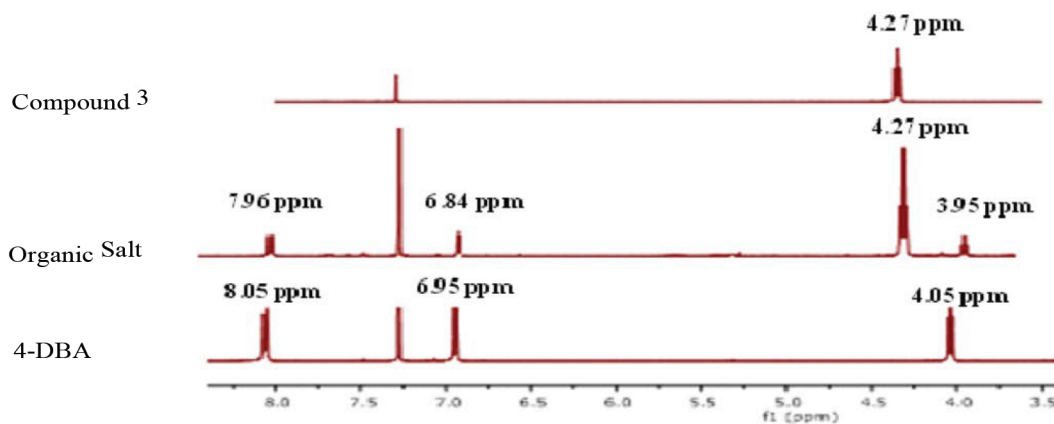


Figure 1. FT-IR spectra of compound 3, organic salt, and benzoic acid (4-DBA).

The interaction between the s-triazine and a carboxyl group of the mesogenic unit was also examined using NMR spectroscopy. The signals corresponding to the aromatic hydrogens of the benzoate unit shift from 8.05 ppm and 6.95 ppm to 7.96 ppm and 6.84 ppm, respectively. The shift was attributed due to an increase in electron density of the aromatic ring. Likewise, the signals of $-\text{O}-\text{CH}_2-$ hydrogens of 4-DBA in the complex shifted to a higher field, 3.95 ppm. The corresponding signals of pure 4-DBA were observed at 4.05 ppm (Figure 2). Additionally, the triplet signals at 4.27 ppm of compound 3 show no shifting by complexation because their electronic environment did not change.

In addition, the ^{13}C NMR spectra show that the carbonyl carbon shifted from 171.6 to 173.10 ppm. This change in chemical shift is due to a decrease in electron density after the ionic interaction, whereas the aromatic carbon next to the alkoxy group shifts slightly from 163.69 to 163.57 ppm (Figure 3).

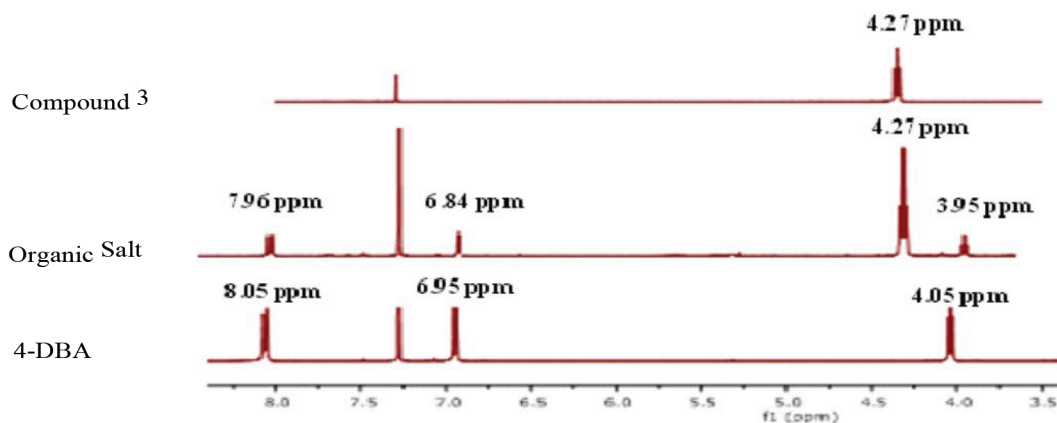


Figure 2. Comparison of the ^1H NMR spectra (in CDCl_3) of compound **3** (triazine compound of organic salt), organic salt **5**, and benzoic acid (4-DBA).

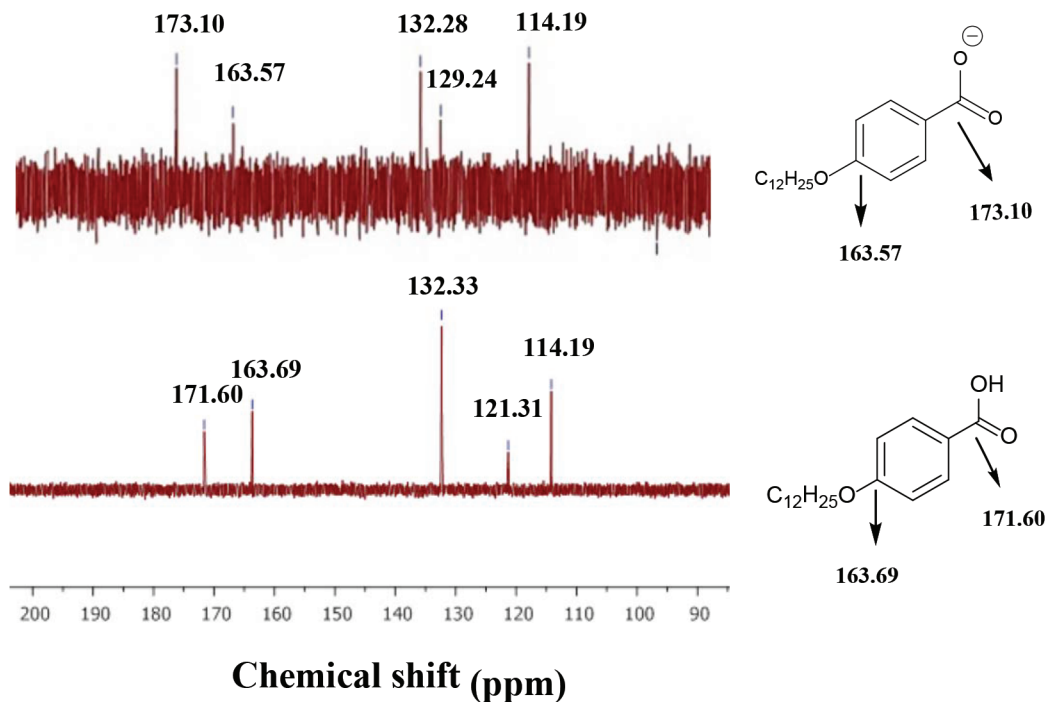


Figure 3. ^{13}C NMR spectra (in CDCl_3) of benzoic acid (4-DBA) (bottom) and organic salt **5** (top).

Additionally, the HRMS spectrum of the salt indicates the presence of M^{5+} at 360.47 and $(\text{M}+5\text{Na})^{5+}$ at 383.4788 peaks, which correspond to $\text{C}_{109}\text{H}_{180}\text{N}_{12}\text{O}_9$ (1802.71, molecular weight of **5**) and $\text{C}_{109}\text{H}_{180}\text{N}_{12}\text{O}_9\text{Na}_5$ (1917.394, pentasodium salt of compound **5**), respectively (Figure 4).

The mesomorphic properties of the star-shaped compound **3** with triazine, 4-DBA, and organic salt (**5**) were investigated using POM and DSC. The phase transition of the corresponding molecules is given in the table. The peak temperatures are given in degrees Celsius and the numbers in parentheses indicate the transition enthalpy (ΔH) in kJ mol^{-1} . As shown in Figure 5, compound **3** shows one endotherm corresponding to crystal to isotropic (Iso) transition in the heating DSC thermogram. Nonmesomorphism of compound **3** was also confirmed by optical polarizing microscope (PM) observation.

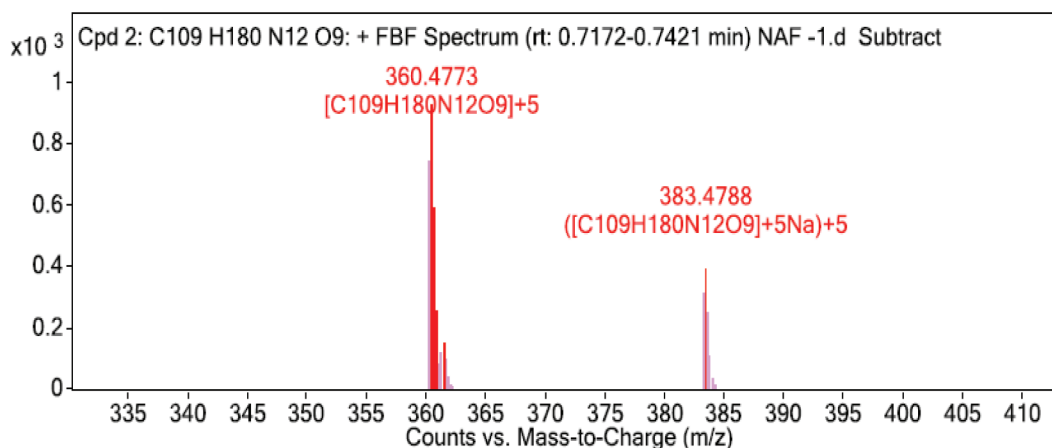


Figure 4. HRMS result of organic salt 5.

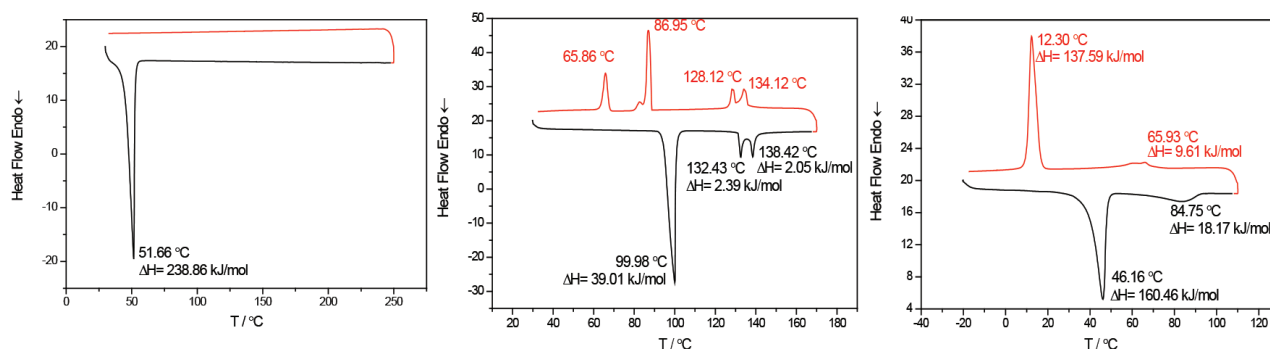


Figure 5. DSC thermograms of (left) compound **3**, (center) 4-DBA, and (right) organic salt (**5**) on 1st heating and cooling ($10 \mu\text{C min}^{-1}$).

Compound 4-DBA, with an *n*-dodecyloxy alkyl chain, shows enantiotropic liquid crystalline properties in agreement with the behavior observed for analogous benzoic acids carrying an alkoxy chain with different numbers of carbon atoms at position 4 of the aromatic ring [16–18]. Upon heating, 4-DBA showed three peaks corresponding to Cr–SmC–N–Iso transitions. On cooling from the isotropic phase, the same behavior of reverse transitions was observed. Furthermore, a calorimetric peak corresponding to Cr–Cr transition at $65.86 \text{ }^\circ\text{C}$ was detected in the cooling DSC thermogram. A typical texture of SmC mesophase observed for 4-DBA is shown in Figure 6 as a representative case.

The organic salt **5** exhibits a phase transition sequence of Cr–Col–Iso, which is in agreement with two endotherms in the DSC heating curves. On cooling from the isotropic liquid, the dendritic growing texture was observed at $67\text{--}20 \text{ }^\circ\text{C}$ (Figure 7). The dendritic growing was composed of a disc-like shaped π -conjugated system based on 1,3,5-triazine central core and the mesogenic carboxyl group, referred to here as the Col phase, which could be considered columns stacked in either rectangular or hexagonal 2D lattices [19–22]. Below about $T = 20.0 \text{ }^\circ\text{C}$, the dendritic texture of the Col phase completely disappears and the crystalline phase starts to appear.

The formation of the columnar mesophase is explained by ionic interaction between the triarmed π -conjugated system and the mesogenic carboxyl group. In this noncovalent intermolecular interaction, the star-shaped compound **3** based on the 1,3,5-triazine acts as a proton acceptor and COOH of 4-DBA with the

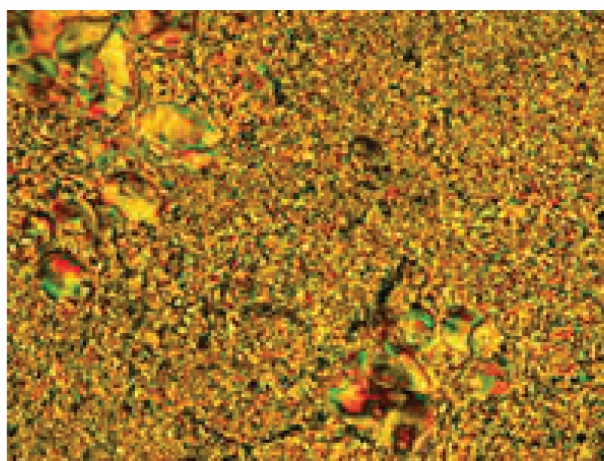


Figure 6. A typical texture of smectic C mesophase of compound 4-DBA $T = 118.0$ °C as observed between crossed polarizers in an ordinary glass plate on cooling.

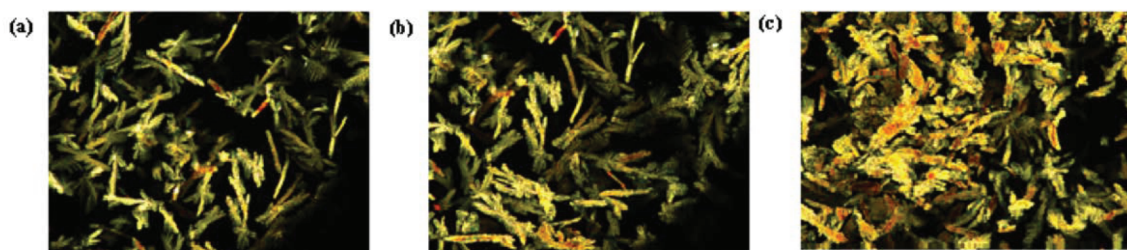


Figure 7. Optical textures of organic salt **5** as observed between crossed polarizers in an ordinary glass plate on cooling; (a) dendritic texture of Col phase at 52 °C and (b) 45 °C; (c) crystalline phase at 20 °C.

Table 1. Mesophases and phase transition temperatures as observed on heating (H \rightarrow) and cooling (\leftarrow C) and corresponding transition enthalpies of the compounds **3**, 4-DBA, and organic salt **5**.

Comp.	T/°C [ΔH kJ/mol] ^a
3	H \rightarrow : Cr 51.66 [<i>238.86</i>] Iso
4-DBA ^b	H \rightarrow : Cr 99.98 [<i>39.01</i>] SmC 132.43 [<i>2.39</i>] N 138.42 [<i>2.05</i>] Iso
OS (5)	H \rightarrow : Cr 46.16 [<i>160.46</i>] Col 84.75 [<i>18.17</i>] Iso Cr 12.30 [<i>137.59</i>] Col 65.93 [<i>9.61</i>] Iso: \leftarrow C

^aPerkinElmer DSC-6; enthalpy values in italics in brackets taken from the 1st heating and cooling scans at a rate of 10 °C min^{-1} ; Abbreviations: Cr = crystalline, SmC = tilted smectic phase, N = nematic phase; Col = columnar mesophase, Iso = isotropic liquid phase. ^b[16,17] Cr 95.1 SmC 128.9 N 137.2 Iso [18] Cr 92.4 SmC 131.5 N 142.0 Iso

n-dodecyloxy terminal chain as the proton donor. The resultant ionic interaction has a striking influence on mesogenic properties such as melting and clearing temperatures as well as inducing a columnar phase at lower temperatures.

4. Conclusion

We prepared and characterized a π -conjugated macromolecular structure composed of a 1,3,5-triazine central core and 1,3,5-triazine rings carrying dodecyloxy chains, which are positioned at the peripheries of the central core by acetylenic bridges, and investigated the properties of the LC of its benzoate salt. The organic salt

that was made between the π -conjugated system and 4-dodecyloxy benzoic acid exhibited an enantiotropic Col phase with a dendritic texture at lower temperatures close to room temperature.

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