

Six-Armed Structures Based on Benzene Ring, Synthesis and Characterization via Sonogashira Coupling

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Abstract: New six-armed compounds consist of benzene ring as a central core substituted with aromatic ring and three rod-like armed of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine as the peripheral arms unit which were obtained by sequential nucleophilic substitution of chlorine atoms in cyanuric chloride. The substitution took place at the acetylenic periphery on the central benzene ring by cross-coupling. Equimolar mixtures of the six-armed compounds based on the benzene core with the complementary 4-dodecyloxybenzoic acid, which already possessed liquid crystal property, resulting in the organic salt. The organic salts and structures were investigated by differential scanning calorimetry (DSC) and confirmed by spectroscopic methods (¹H-NMR, ¹³C-NMR, Mass spectrometry, and FT-IR).

Keywords: triazine; liquid crystals; hydrogen bonding; benzene core derivatives; synthesis; characterization

■ INTRODUCTION

Multi-arm liquid crystals exhibited very specific electro-optical phenomena and wide applications [1-2]. Chiral liquid crystalline materials use in flexible color display applications [3-5]. Branched-arm LCs have a higher molecular weight in comparing with the conventional low molecular mass compounds, which usually contain a core and a few mesogenic units as the side arm; that is why it attracted much attention for their special molecular structures and interesting properties. Derivatives of benzene [6-8], condensed aromatic rings [9], are often used as cores of the multi-arm compounds. The multi-arm liquid crystal shows different properties such as lower melting temperature, lower viscosity, good solubility, etc., from the linear dimers, trimers, and oligomers [10-12]. One of the most interested classes in the liquid crystal is the star-shaped, which has been paid much attention in recent years [13-16].

Heterocycles are important in the design and synthesis of organic functional materials, especially in the development of thermotropic liquid crystals, since phase structure, polarity, geometry, luminescence, and many other molecular properties can be varied by the introduction of heteroatoms [17-20]. In recent years, much interest focus on the synthesis and characterization of compounds containing a 1,3,5-triazine unit or used as a central core due to their interesting properties, such as liquid crystalline and nonlinear optical properties as well as their applications in other fields [21-24]. The 1,3,5-triazine is an electron-accepting unit, which can be substituted at the 2,4,6-positions with an appropriate aromatic rigid core through linking groups at the side arms to give a C₃-symmetrical system (star-shaped) that is able to form columnar mesophases [25]. Moreover, the extension of the electronic conjugation of these types of mesogens

should give CLCs with luminescent properties and high charge-carrier mobility [26-27].

Supramolecular liquid crystals (LCs), obtained via intermolecular hydrogen bonding have attracted considerable attention due to their ability of existence of the mesophase. In these cases, the hydrogen bonded complexes are formed between two identical molecules, and the system can be considered as self-complementary [28].

In this study, our research focuses on star-shaped molecules bearing three aromatic arms and three rod-like arms of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine as the peripheral arms unit linking through triple bond on the benzene core, started from 1,3,5-trichloro-2,4,6-triiodobenzene, which is derived from 1,3,5-trichlorobenzene and 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine which is derived from 2,4,6-trichloro-1,3,5-triazine. The synthesis of organic salts was obtained via intermolecular hydrogen bonding between six-armed compounds and 4-dodecyloxybenzoic acid, which is already possessed liquid crystal property to increase the possibility of liquid crystalline of the mixture [29].

■ EXPERIMENTAL SECTION

Materials

The reagents and solvents used were obtained from Merck with pro analysis grade without further purification, i.e., cyanuric chloride, dodecan-1-ol, ethynylbenzene, 1,3,5-trichlorobenzene, 2-iodo-thiophene, 2-ethynylbenzene, ethynyltrimethylsilane, copper iodide, potassium carbonate, tetrakis (triphenylphosphine)palladium and triethylamine, tetrahydrofuran, dimethylformamide, and dioxane. Thin-layer chromatography was performed using aluminum plates (20 × 20 cm) coated with silica gel 60 F254 (Merck), while column chromatography was carried out using silica gel 60 (0.063–0.200 mm) from Merck.

Instrumentation

Structure elucidation of compounds was carried out using HRMS (High resolution mass spectrometry), FT-IR (Shimadzu Prestige-21, KBr discs), ¹H-NMR (500 MHz) and ¹³C-NMR (125 MHz) (CDCl₃, standard internal TMS) spectrometers. Liquid crystalline evaluation of the organic

salts was performed using DSC (Differential scanning calorimetry).

Procedure of Six-armed Compounds

2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (2)

A mixture of 2,4,6-trichloro-1,3,5-triazine (1) (1.90 g, 10.3 mmol), dodecan-1-ol (3.84 g, 20.6 mmol) and K₂CO₃ (2.84 g, 20.6 mmol) were dissolved in 10.0 mL of THF (Scheme 2). The mixture was stirred at 50 °C for 5 h under argon atmosphere. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product was purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to give white solid materials with a yield (3.50 g, 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 173.17 (O-C_{het}), 172.18 (Cl-C_{het}), 68.54 (OCH₂), 31.95, 29.68, 29.66, 29.61, 29.56, 29.38, 29.33, 28.68, 25.86, 22.72, 14.14). HRMS = *m/z* M⁺ and [M+K]⁺ calcd for C₂₇H₅₀ClN₃O₂: 483.36; found: 483.35, 523.3282 respectively.

2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (3)

A mixture of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (2) (1.20 g, 2.47 mmol), K₂CO₃ (0.40 g, 22.0 mmol), ethynyltrimethylsilane (0.29 g, 2.96 mmol), Pd(PPh₃)₄ (0.28 g, 0.24 mmol), CuI (0.09 g, 0.49 mmol), were dissolved in 10.0 mL of THF (Scheme 2). The mixture was refluxed for 6 h under argon atmosphere. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated to give brown oily material with a yield (1.10 g, 81%). HRMS = *m/z* [M+H]⁺ calcd for C₃₂H₅₉N₃O₂Si: 545.44; found: 546.39.

Trimethyl(thiophen-2-ylethynyl) silane (5)

A mixture of 2-iodothiophene (4) (0.40 g, 1.90 mmol), K₂CO₃ (0.394 g, 2.85 mmol), 2-methylbut-3-yn-2-ol (0.17 g, 2.09 mmol), Pd(PPh₃)₄ (0.021 g, 0.019 mmol), CuI (0.007 g, 0.038 mmol), were dissolved in 10.0 mL of

THF under argon atmosphere (Scheme 2). The mixture was refluxed for 6 h. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated to give brown oily material with a yield (0.27g, 87%). HRMS = m/z $[M+H]^+$ calcd for $C_9H_{10}OS$: 166.0; found: 167.05.

2-ethynylthiophene (6)

A mixture of trimethyl(thiophen-2-ylethynyl) silane (5) (0.25 g, 1.38 mmol) and K_2CO_3 (0.249 g, 1.80 mmol) were dissolved in 10.0 mL of toluene (Scheme 2). The mixture was stirred for 12 h at 80 °C. The solution was poured into a mixture of dichloromethane (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated to give brown oily material with a yield (0.1 g, 83%). HRMS = m/z $[2M^+]$ calcd for C_6H_4S : 108; found: 108.

1,3,5-trichloro-2,4,6-triiodobenzene (8)

Periodic acid (3.00 g, 13.2 mmol) was added slowly to 50.0 mL of concentrated sulfuric acid and stirred for 1 h then Potassium iodide (6.50 g, 39.5 mmol) was added to the mixture slowly at 0 °C, after the reaction reached room temperature, 1,3,5-trichlorobenzene (7) (0.789 g, 4.38 mmol) was added (Scheme 3). The solution was poured into a mixture of ethyl acetate (50.0 mL) and water (50.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated to give light yellow solid materials with a yield (1.50 g, 62%), MP. 280 °C. HRMS = m/z M^+ and $[M+H]^+$ calcd for $C_6Cl_3I_3$: 557.6; found: 558.6.

((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tribenzene (9a)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (8) (0.50 g, 0.90 mmol), ethynylbenzene (0.28 g, 2.68 mmol), Pd (PPh_3)₄ (0.01 g, 0.09 mmol), CuI (0.03 g, 0.18 mmol) and K_2CO_3 (0.28 g, 2.86 mmol) were dissolved in 10.0 mL of dioxane (Scheme 3). The mixture was stirred at 75 °C for 6 h under argon atmosphere. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product was purified by column chromatography

with hexane/ethyl acetate (5% EtOAc) as an eluent to give white powder with a yield (0.35 g, 81%). MP. 140–145 °C. ¹H-NMR (500 MHz, $CDCl_3$) (7.6 (m, 1H), 7.4 (m, 2H). ¹³C-NMR (142, 132.5, 129.2, 128.5, 121.8, 81.6, 74). HRMS = m/z $[M+H]^+$ calcd for $C_{30}H_{15}Cl_3$: 481.80; found: 483.02.

2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) trithiophene (9b)

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (8) (0.50 g, 0.89 mmol), 2-ethynylthiophene (6) (0.48 g, 2.69 mmol), Pd (PPh_3)₄ (0.10 g, 0.089 mmol), CuI (0.03 g, 0.178 mmol) and K_2CO_3 (0.39 g, 2.84 mmol) were dissolved in 10.0 mL of dioxane (Scheme 3). The mixture was stirred at 75 °C for 6 h under argon atmosphere. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product was purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to give pale yellow powder with a yield (0.37 g, 84%), MP. 124–127 °C. ¹H-NMR: ($CDCl_3$) (7.3 (m, 1H) 3× (1H), 7.17 (m, 1H) 3× (1H), 6.7 (dt, J = 6.8, 3.4 Hz, 1H) 3× (1H)), ¹³C-NMR: (146, 141, 138, 132, 131, 129, 100, 98). HRMS = m/z M^+ and $[M+H]^+$ calcd for $C_{24}H_9Cl_3S_3$: 499.88; found: 499.89 and 500.88, respectively.

6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (10a)

((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene (9a) (0.15 g, 0.31 mmol), 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (3) (0.51 g, 0.93 mmol), Pd(PPh_3)₄ (0.035 g, 0.031 mmol), CuI (0.011 g, 0.06 mmol) and K_2CO_3 (0.136 g, 0.99 mmol) were dissolved in 10.0 mL of dioxane (Scheme 3). The mixture was stirred at 80 °C for 16 h under argon atmosphere. The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product was purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to obtain light brown with a yield (0.42 g, 75%). ¹H-NMR: ($CDCl_3$) (7.3 (dt, J = 11.1, 5.4 Hz, 6H), 7.18 (m, 9H), 4.15 (t, J = 6.8 Hz, 12H, OCH_2), 1.64–1.50 (m, 12H, CH_2), 1.44–1.1 (m, 108H, CH_2), 0.7 (t, J = 6.8 Hz, 18H, CH_3). ¹³C-NMR: (173, 171, 142, 139, 132, 129, 128, 122, 108, 98, 81,

74, 68, 32, 31, 30, 29, 28, 24, 22, 12). MS = m/z $[M+2]^+$ calcd for $C_{117}H_{165}N_9O_6$: 1793.6; found: $896.64 \times 2 = 1793.28$.

6,6',6''-((2,4,6-tris(thiophen-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (10b)

2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))trithiophene (**9b**) (0.15 g, 0.3 mmol), 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**3**) (0.49 g, 0.90 mmol), $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol), CuI (0.011 g, 0.06 mmol) and K_2CO_3 (0.13 g, 0.96 mmol) were dissolved in 10.0 mL of dioxane (Scheme 3). The mixture was stirred at 80 °C for 16 h under argon atmosphere. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer after separation was dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product was purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to obtain light brown with a yield (0.41g, 76%). 1H -NMR: ($CDCl_3$) (7.25 (m, 6H), 6.95 (d, 3H), 4.3 (t, $J = 6.8$ Hz, 12H, OCH_2), 1.6 (m, 12H, CH_2), 1.4–1.1 (m, 108H, CH_2), 0.8 (t, $J = 6.8$ Hz, 18H, CH_3). ^{13}C -NMR: (173, 166, 162, 134, 131, 128, 127, 121, 114, 98, 87, 68.5, 32, 31, 30, 29, 28, 24, 22, 12). HRMS = m/z $[M+2H]^{+2}$ calcd for $C_{111}H_{159}N_9O_6S_3$: 1811.7; found: $(906.58 \times 2 - 2 = 1811.16)$.

Second route of synthesis compounds 10(a-b): 6,6',6''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis(dodecyloxy)-1,3,5-triazine) (11)

1,3,5-trichloro-2,4,6-triiodobenzene (**8**) (0.50 g, 0.89 mmol), 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**3**) (1.47 g, 2.69 mmol), K_2CO_3 (0.39 g, 2.84 mmol), $Pd(PPh_3)_4$ (0.01 g, 0.089 mmol), CuI (0.033 g, 0.178 mmol), were dissolved in 10.0 mL of dioxane under argon atmosphere (Scheme 4). The mixture was stirred at 70 °C for 12 h. The solution was poured into a mixture of ethyl acetate (20.0 mL) and water (20.0 mL). The organic layer was washed and dried over sodium sulphate. The solvent was removed under vacuum to give yellow solid material with yield (1.10 g, 76%). 1H -NMR: ($CDCl_3$) (4.3 (t, 12H, OCH_2), 1.65 (m, 4H, CH_2), 1.35 (m, 18H, CH_2), 0.95 (t, 6H, CH_3). ^{13}C -NMR (173.5, 171.3, 145.6, 126.100.3, 97.89, 68.5, 31.9, 29.65, 29.6, 29.5, 29.3, 28.6, 25.8, 22.7, 14.1). HRMS = m/z $[M+2]$ and $[M+2(NH_4)]^{+2}$ calcd

for $C_{93}H_{150}Cl_3N_9O_6$: 1594.1; found: 797.52 ($797.52 \times 2 = 1595.04$), 816.09 ($816.09 \times 2 - 36 = 1596.1$) respectively.

4-(dodecyloxy) benzoic acid (4-DBA) (12)

A solution of 4-hydroxy benzoic acid (8.20 mmol), 1-bromododecane (5.50 mL, 23.0 mmol, 2.8 eq) and KOH (1.30 g, 23.0 mmol, 2.8 eq) in ethanol (25.0 mL) was heated under reflux for 2 days (Scheme 5). By adding 10% aqueous KOH (25.0 mL) to the mixture and refluxed overnight, the hydrolysis was carried out. After cooling down, the reaction mixture was acidified with HCl (6.0 M), the precipitate was filtered, washed with water and recrystallized from ethanol to obtain the pure product 4-dodecyloxybenzoic acid, a white solid material with yield (4.55 g, 91%). 1H -NMR (500 MHz, $CDCl_3$) showed peaks at (δ 8.10 (d, 2H), 6.98 (d, 2H), 4.07 (t, 2H), 1.84 (m, 2H), 1.48 (m, 2H), 1.37–1.28 (m, 16H), 0.91 (t, 3H). The FT-IR (2914, 2848, 2559, 1670, 1604) cm^{-1} .

Synthesis of organic salt

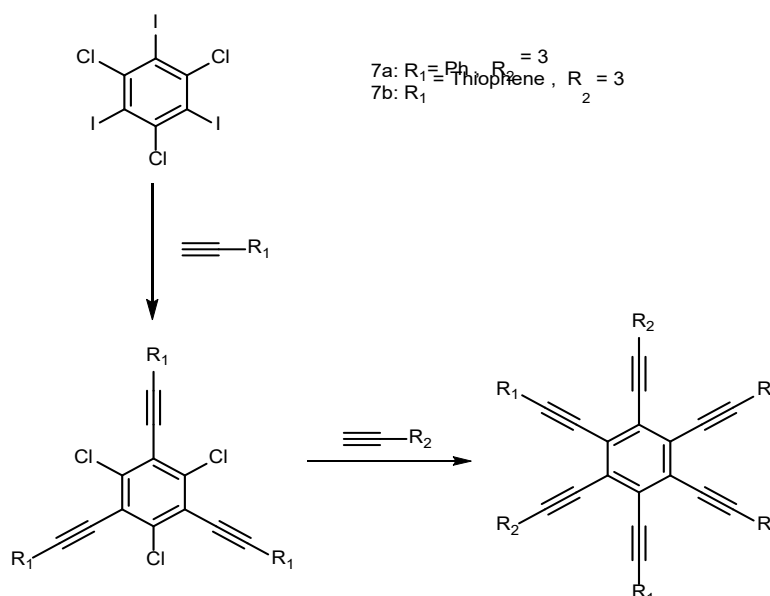
4-DBA mesogenic unit (**12**) with a carboxyl group was added into a solution of compound **10 (a-b)** in 10 mL of dry THF with one to one ratio (Scheme 5). The resulting solution was sonicated for 15 min until a transparent solution was observed. Then, the solvent was removed in vacuum.

The organic salt (13a). 1H -NMR (7.9 (d, 2H), 7.4 (d, 2H), 7.15 (m, 3H), 6.8 (d, 2H), 4.2 (t, 12H, OCH_2), 3.85 (t, (OCH_2), 1.75 (m, 12H, CH_2), 1.15 (m, 108H, CH_2), 0.7 (t, $J = 7.0$ Hz, 18H, CH_3). FT-IR (2917, 2855, 2564, 1694, 1609, 1560, 1477, 1419, 1332, 1274). MS = m/z $[M+3(HCOO)]^{-3}$ calcd for $C_{136}H_{195}N_9O_9$: 2098.5; found: 744.496 ($744.496 \times 3 - 3 \times 45 = 2098.48$).

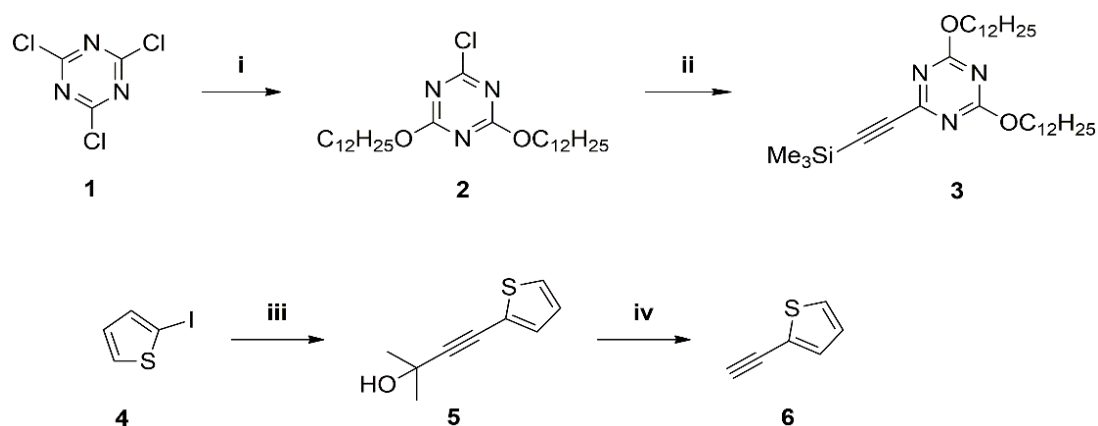
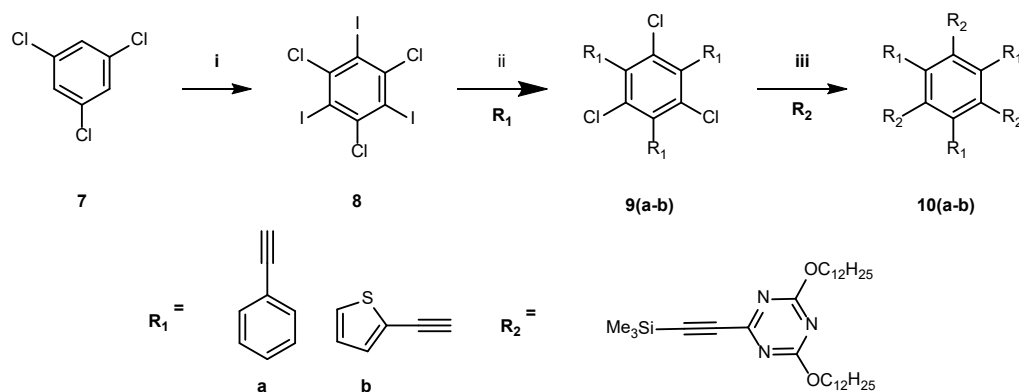
The organic salt (13b). 1H -NMR (7.85 (d, 2H), 7.25 (m, 2H), 6.95 (d, 1H), 6.75 (d, 2H), 4.26 (t, 12H, OCH_2), 3.8 (t, (OCH_2), 1.75 (m, 12H, CH_2), 1.3–1.15 (m, 108H, CH_2), 0.75 (t, 18H, CH_3). FT-IR (2915, 2844, 1680, 1584, 1530, 1560, 1490, 1419, 1278, 1156).

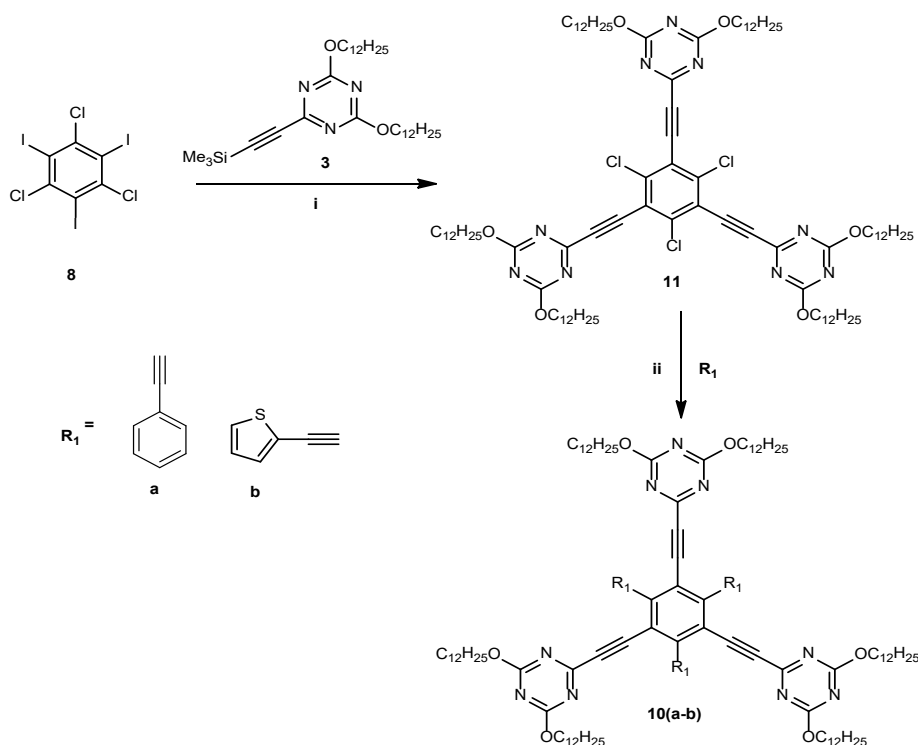
RESULTS AND DISCUSSION

In this contribution, six arms structures based on benzene ring were synthesized via Sonogashira-reaction using different substituted started with 1,3,5-trichlorobenzene and 2,4,6-trichloro-1,3,5-triazine as described in (Scheme 1-5). The structures were confirmed

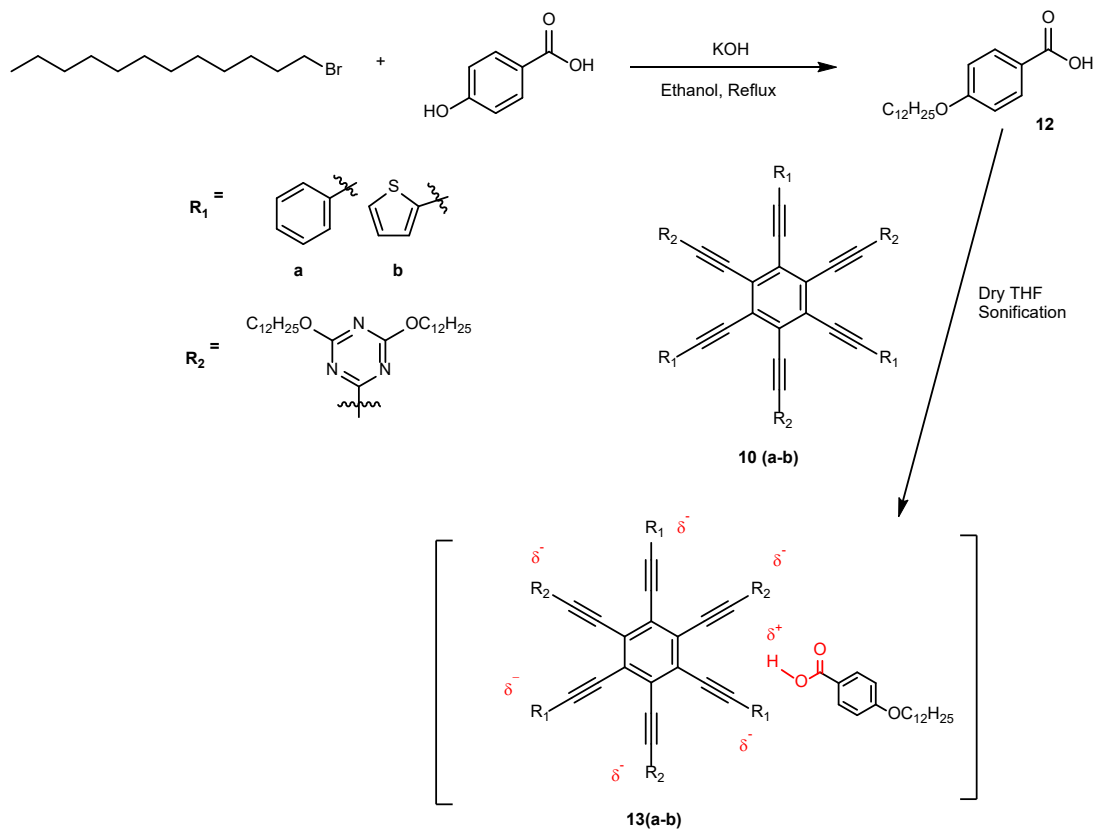


Scheme 1. Synthesis route of six arms compounds

Scheme 2. Synthesis route of intermediate compounds. Reaction and condition: **i)** K_2CO_3 , dodecan-1-ol, $0-50^\circ\text{C}$, 5 h, THF, **ii)** Ethynyltrimethylsilane, K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, CuI, THF, Reflux, **iii)** 2-methylbut-3-yn-2-ol, $\text{Pd}(\text{PPh}_3)_4$, CuI, K_2CO_3 , THF, Reflux, **iv)** K_2CO_3 , toluene, 80°C , 12 hScheme 3. Synthesis route of six arms on the benzene ring. Reaction and condition: **i)** H_5IO_6 , H_2SO_4 , KI, 0°C 10.0 min, r.t., **ii)** $\text{Pd}(\text{PPh}_3)_4$, CuI, Et_3N (3.2 eq), Dioxane, 75°C , 6 h, **iii)** $\text{Pd}(\text{PPh}_3)_4$, CuI, K_2CO_3 , Dioxane, 80°C , 12 h



Scheme 4. Synthesis route of six arms compounds **10(a-b)**. Reaction and condition: **i**) Pd (PPh₃)₄, CuI, K₂CO₃, Dioxane, 70 °C, 6 h, **ii**) Pd(PPh₃)₄, CuI, K₂CO₃, Dioxane, 80 °C, 12 h



Scheme 5. Synthesis procedure of organic salt **13(a-b)**

by spectroscopic analysis and investigated by differential scanning calorimetry (DSC).

The compounds (**10a**, **10b**) were obtained in two routes (Scheme 3, Scheme 4). In comparison, the yield of product in the second route was higher than the first route, which may occur due to the chloride that has more reactivity to couple with aromatic (ethynylbenzene, 2-ethynylthiophene) than to couple with 2,4-bis(dodecyloxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine, and the reaction to achieve the product was also shorter as well [30] (Table 1).

The formation of ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FTIR. The sharp peak belongs to the carboxylic (Fig. 1). Moreover, asymmetric stretching carboxylate peak at 1670 cm^{-1} of pure 4-DBA was shifted in both organic salt to 1680 cm^{-1} and 1694 cm^{-1} , respectively, after ionic interaction. In addition, peaks at 2900 and 2800 cm^{-1} are belonged to hydrogen stretching.

The formation of ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was also checked by NMR spectroscopy. The signals corresponding to the aromatic protons of alkoxy benzoate unit shift to (7.95, 6.8) ppm in compound (**13a**) and (7.85, 6.75) ppm in compounds (**13b**) comparing to pure 4-DBA signals at (8.05, 6.95) ppm — these shifting due to an increase in electron density of the aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.85 ppm in compound (**13a**) and 3.8 ppm in compound (**13b**) as

compared with the signals of pure 4-DBA at 4.05 ppm (Fig. 2). Additionally, the oxymethylene protons and aromatic protons of both organic salts show no shifting since their electronic environment did not change.

Additionally, unambiguous support for the structures of (**13a**), came from the QTOF analysis. The mass spectra of the organic salt indicate the presence of $[M+3(\text{HCOO})]^{-3}$ at 744.496 and 744.84, as seen in Fig. 3.

Compound 4-DBA, which has an n-dodecyloxy terminal chain, shows enantiotropic liquid crystalline properties that are in agreement with the behavior observed for analogous benzoic acids carrying an alkoxy chain with the different numbers of carbon atoms at 4-position of the aromatic ring [31-33]. 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. In addition to this, a calorimetric peak corresponding to Cr-Cr transition at $65.86\text{ }^{\circ}\text{C}$ was detected in the cooling DSC thermogram (34). A typical texture of the SmC mesophase observed for 4-DBA is shown in Fig. 4.

Table 1. Comparison of the percentage yield

Comp. 10(a-b)	R ₁	R ₂	Time/h	Yield/%
Scheme 3	9a	3	16	75
	9b	3	16	76
Scheme 4	11	ethynylbenzene	12	85
	11	2-ethynylthiophene	12	81

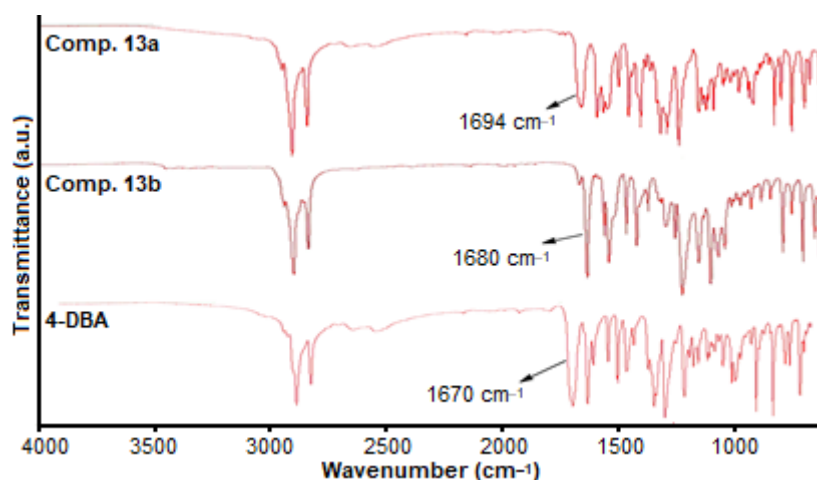


Fig 1. FT-IR spectra of organic salt (**13a**, **13b**) and benzoic acid (4-DBA)

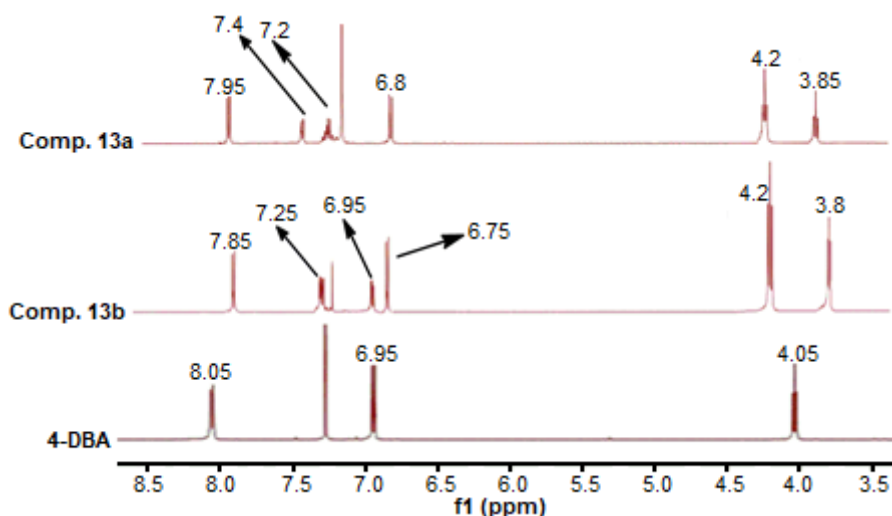


Fig 2. The comparison of $^1\text{H-NMR}$ spectra (in CDCl_3) of organic salts (13a, 13b) and benzoic acid (4-DBA)

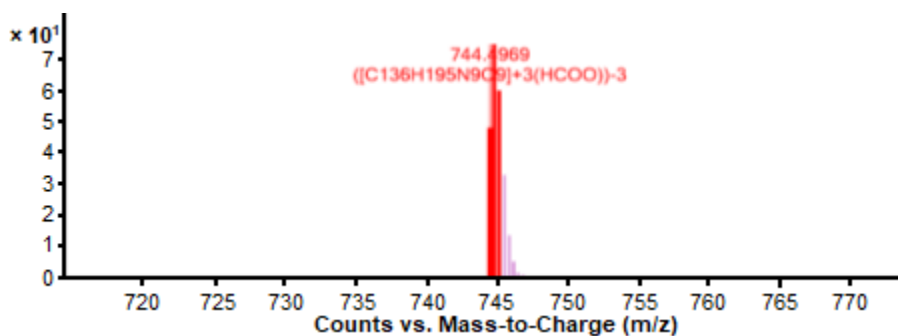


Fig 3. Q-TOF LC/MS result of organic salt (9a)

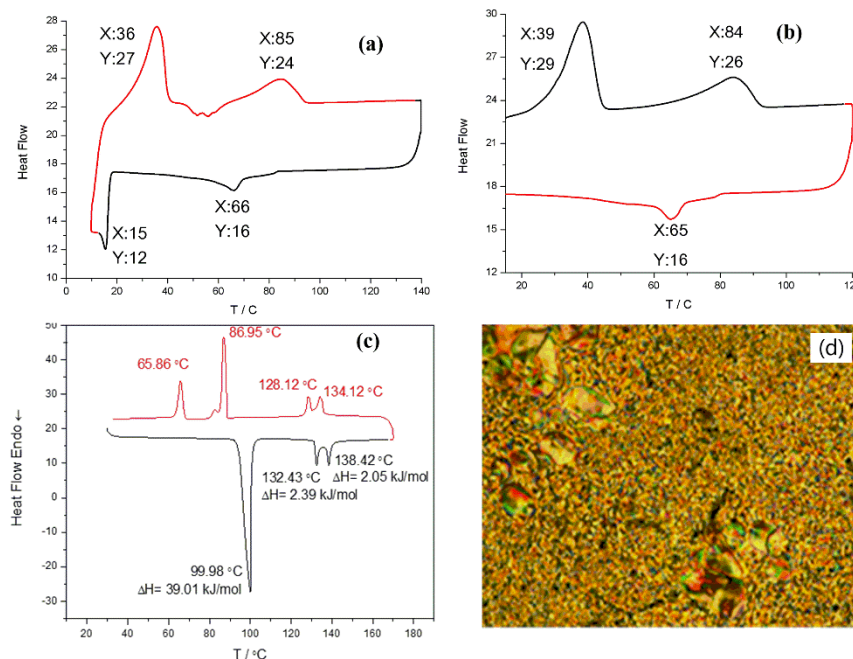


Fig 4. (a) DSC thermograms of (a) **organic salt 13a**, (b) **organic salt 13b**, (c) **4-DBA** on 1st heating and cooling ($10 \text{ }^\circ\text{C min}^{-1}$), (d) A typical texture of the smectic C mesophase of compound **4-DBA** $T = 118.0 \text{ }^\circ\text{C}$ as observed between crossed polarizers in ordinary glass-plates on cooling

Table 2. Mesophases and phase transition temperatures as observed on heating (H→) and cooling (←C) and corresponding transition enthalpies of the organic salts **13a**, **13b**, and **4-DBA**

Comp.	T/°C [ΔH kJ/mol]
4-DBA ^b	H →: Cr 99.98 [39.01] SmC 132.43 [2.39] N 138.42 [2.05] Iso
OS (13a)	H →: Cr 12 [14.9] Col 16 [66] Iso: ← C Cr 29.3 [38.7] Col 25.6 [83.6] Iso: ← C
OS (13b)	H →: Cr 15.7 [65.2] Cr 27 [36] Col 23.9 [84.9] Iso: ← C

^aPerkin-Elmer 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
[31-32] Cr 95.1 SmC 128.9 N 137.2 Iso
[33] Cr 92.4 SmC 131.5 N 142.0 Iso

The transition phase determined by differential scanning calorimetry (DSC), organic salt **13a**, exhibits a phase transition, which is in agreement with two endotherms in the DSC heating curves. On heating, two peaks were observed at 84–27 °C. On the cooling form, the isotropic liquid, two peaks corresponding to the transition phase were observed at 66–15 °C, as shown in Fig. 4. However, for the organic salt **13b**, on heating, two endotherm peaks were observed at 83–38 °C, whereas in the cooling cycle, one peak was observed at 65 °C, the results were summarized in (Table 2).

Both organic salts with multi-side chains, the differential scanning calorimetry revealed textures suggesting liquid crystalline states below the transitions at higher temperatures. An increase in the length of the alkoxy side chains leads to a steady decrease in the temperatures for the phase transition [35].

By the differential scanning calorimetry (DSC), two endothermic peaks were observed in the heating and cooling cycle of the compound **13a**, which expected to exhibit liquid crystal phases (Fig. 4). Besides, compound **13b** also showed two endothermic peaks in the heating cycle but showed one peak only in the cooling cycle, which may also exhibit a transition phase.

■ CONCLUSION

A new six arms compounds based on benzene ring as a central core substituted with different aromatic compounds and three rod-like armed of 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine, using 2,4,6-trichloro-

1,3,5-triazine and 1,3,5-trichlorobenzene in the presence of palladium catalyst through the cross-coupling was efficiently synthesized. The structures were investigated by differential scanning calorimetry (DSC) and confirmed by the spectroscopic analyses (¹³C-NMR, ¹H-NMR, and MS). The compounds were evaluated for their liquid crystal's behaviors. The results from the DSC suggested that liquid crystals behaviors of both organic salt at low temperatures are due to the ionic interaction with the complementary of 4-dodecyloxybenzoic acid, which already possessed a liquid crystal at low temperatures.

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