NOVA SÍNTESE E CARACTERIZAÇÃO DE ESTRUTURAS MACROMOLECULARES

NEW MACROMOLECULAR STRUCTURES SYNTHESIS AND CHARACTERIZATION

JABBAR, Adel Ismael^{*1}, RAWI, Rehab Ayal², ABDULHAMEED, Jasim Mohammed³

^{1,2,3}Ministry of Education, Al-Anbar, Iraq

^{*} Corresponding author

e-mail: adilwaleed@yahoo.com

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RESUMO

Os cristais líquidos são únicos em suas propriedades e usos e têm um papel essencial na área de aplicações tecnológicas como elétrica, ótica, *display*, mapa de temperatura e materiais de comutação. Este estudo teve como objetivo sintetizar derivados de hexaetnilbenzeno a partir de 1,3,5-triclorobenzeno benzeno como núcleo central substituído por três anéis aromáticos e três armados de 2-cloro-4,6-bis ((3,7-dimetiloct-6-en-1-il) oxi) -1,3,5-triazina. Essas moléculas são formadas pela ligação covalente de três braços simetricamente a um núcleo central que podem ser ligados ao núcleo central através de ligantes flexíveis, semiflexíveis ou rígidos. A substituição ocorre na periferia acetilênica no anel central do benzeno e foi obtida com eficiência pelo acoplamento Sonogashira. Os compostos de seis braços baseados no núcleo do benzeno foram misturados com a razão complementar 1:1 do ácido 4-dodeciloxibenzóico, que já possuía propriedades de cristais líquidos para aumentar a possibilidade de formação destes resultando em um sal orgânico. Os sais orgânicos obtidos foram investigados quanto ao seu comportamento em cristal líquido por microscopia óptica de polarização (POM) e calorimetria de varredura diferencial (DSC). Todos os compostos intermediários e finais foram confirmados por técnicas espectroscópicas (1H RMN, 13C RMN e espectrometria de massa).

Palavras-chave: *Triazina, Cristais líquidos, Ligação de hidrogênio, Síntese e Caracterização.*

ABSTRACT

Liquid crystals are unique in their properties and use and has an essential role in the area of technological applications such as electrical, optical, displays, temperature maps, and switching materials. This study aimed to synthesize hexaethynylbenzene derivatives starting from 1,3,5-trichlorobenzene benzene as a central core substituted with three aromatic ring and three armed of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine. These molecules are formed by the covalent linking of three arms symmetrically to a central core which may be attached to the central core through flexible, semi-flexible or rigid linkers. The substitution occurred at the acetylenic periphery on the central benzene ring and was achieved efficiently by Sonogashira coupling. The six-armed compounds based on the benzene core was mixed with the complementary 4-dodecyloxybenzoic acid 1:1 ratio, which already possessed liquid crystal property to increase the formation of these resulting in an organic salt. The obtained organic salts were investigated for their liquid crystal behaviour by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). All the intermediate and final compounds were confirmed by spectroscopic techniques (1H NMR, 13C NMR, and mass spectrometry).

Keywords: *Triazine, Liquid crystals, Hydrogen bonding, Synthesis and Characterization.*

1. INTRODUCTION:

Liquid crystal displays (LCDs) are omnipresent in the modern world, representing probably the most prevalent, developed, and profitable technology of thermotropic liquid crystals (Bremer, 2013; Kato, 2018). This application is based on their sensitivity to external electric and magnetic fields, when molecules align fast and at low voltages. This property was the basis for their use in other exciting applications,

especially as sensors. Because of their fluid nature at a specific temperature, liquid crystals (LCs) are very easy to process in thin films, along with maintaining optical properties characteristic to crystalline materials, as the ability to rotate the polarized light plane (birefringence) (Scutaru, 2018).

The chemistry of triazine has gained much increased in the last few decades, due to their applications in organic synthesis and liquid crystal properties (Akkurt *et al.*, 2019). Hexa-

ethynylbenzene derivatives are interested molecular as liquid crystals (Praefcke, 1991; Al-Jumaili, 2020), nonlinear optical material (Kondo, 1995), core structures for dendritic (Kayser, 1999), light-harvesting materials (Mongin, 2000), and building blocks for two-dimensional carbon networks (Kehoe, 2000; Wan, 2000).

Substituted hexa-ethynylbenzenes, in which the ethynyl ends possess different functional groups, are attractive because it would be possible to change the above properties by modifying the substitution pattern of the terminal groups (Sonoda, 2001). The more frequently utilized nucleophilic substitution reactions have been mostly limited to amines and alcohols so far, providing selective substitution at the price of decreased cycloaddition ability due to the electron-donating nature of the new substituent (Boger, 1998; Sakya, 1997; Novák, 2003).

Organic π -conjugated systems, small molecules (Chow, 2014) and polymers, (Tan, 2020) are of great interest for sensing, optical and electronic applications (Usta, 2014). The group of discotic liquid crystals (DLC) offers the additional feature of self-organization, often as a columnar arrangement resulting in anisotropic properties, e.g. one-dimensional charge transport in the liquid-crystalline phase (Kaller, 2012).

Typical DLCs consist of electron-rich polycyclic aromatic units, e.g., triphenylene or hexabenzocoronene, (Kumar, 2005), whereas DLCs with an electron-deficient core are rather scarce (Kestemont, 2001). π -conjugated N-heterocyclic molecules with peripheral aliphatic chains can easily be functionalized to present highly ordered columnar mesomorphism, which results in exciting properties like one-dimensional (1D) high charge carrier mobilities regarding scientific and technological aspects (Gsänger, 2010; Sergeyev, 2007; Demus, 2011).

In the present study on the construction of extended π -electronic systems, it was performed the design and synthesis of new hexaethynylbenzene derivatives starting from 1,3,5-trichlorobenzene benzene as a central core substituted with three aromatic ring and three armed of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine. These molecules are formed by the covalent linking of three arms symmetrically to a central core (scheme 1). These arms may be linked to the central core through flexible or semi-flexible or rigid linkers. When the central core connecting to the linkers and three rigid arms, shape persistent star-shaped mesogens are obtained (Lehmann, M. 2009).

These molecules lack the shape anisotropy of discotic required to exhibit mesophases. Still, their ability to form mesophases is supported by the nanophase segregation of chemically or physically different molecular subunits and their tendency to fill the space efficiently in bulk (Pradhan, 2016). The advantage of six-armed design with concerning to discotic is the synthetic flexibility of the liquid crystal behaviour (Bisoyi, 2010).

Therefore, this study aimed to synthesize hexaethynylbenzene derivatives starting from 1,3,5-trichlorobenzene benzene as a central core substituted with three aromatic ring and three armed of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine.

Scheme 1. Synthesis route of six arms compounds.

2. MATERIALS AND METHODS:

2.1. Chemical and Reagents

Cyanuric chloride, dodecan-1-ol, ethynylbenzene, 1,3,5-trichlorobenzene, 2-iodothiophene, 2-ethynylpyridine, ethynyltrimethylsilane, copper iodide, potassium carbonate, tetrakis(triphenylphosphine)palladium and triethylamine. The solvents were used dry (THF, Dioxane) were obtained from distilling over phosphorous pentoxide (merck).

2.2. Measurement

Purity of the compounds was checked by TLC on silica gel 60 F₂₅₄ (Merck). Synthesized compounds are characterized by ¹H NMR and ¹³C NMR spectra using CDCl₃ as a solvent with TMS as an internal standard. IR spectra were recorded in KBr on a Shimadzu FTIR 8400S spectrophotometer. Mass spectra were recorded on a GCMS-QP 1000 mass spectrometer.

2.3. 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine (2)

2,4,6-trichloro-1,3,5-triazine (**1**) (0.29 g, 1.6 mmol), 3,7-dimethyloct-6-en-1-ol (0.5 g, 3.2 mmol) and K_2CO_3 (0.45 g, 3.2 mmol) were dissolved in 10 mL of THF under argon atmosphere and stirred at 50 °C overnight (Scheme 2). The solution was poured into a mixture of ethyl acetate (10 mL) and water (10 mL). The organic layer after separation dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (2.5% EtOAc) as an eluent to give white powder with yield (0.25 g, 41%). 1H NMR (500 MHz, $CDCl_3$) (5.14 (dd, $J = 7.1, 1.3$ Hz, 2H), 4.5 (m, 4H, OCH_2), 2.09 (m, 4H, CH_2), 1.9 (m, 6H, CH_3), 1.8 (m, 6H, CH_2), 1.6-1.3 (m, 10H, CH_2), 1.07-0.95 (m, 6H, CH_3), ^{13}C NMR (126 MHz, $CDCl_3$) (172, 171, 131.5, 124, 69, 36.8, 35, 29, 25.7, 25.3, 19.2, 17.6). HRMS= M^{+}_{calcd} for $C_{23}H_{38}ClN_3O_2 = 424.27$. $(M+H)^{+}_{found} = 424.27$ and $(M+NH_4)^{+}_{found} = 441.311$ ($441.311 - 18 = 423.3$).

2.4. 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6((trimethylsilyl)ethynyl)-1,3,5-triazine (3)

2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine (**2**) (1.2 g, 2.5 mmol), ethynyltrimethylsilane (0.29 g, 2.96 mmol), K_2CO_3 (0.4 g, 2.96 mmol), $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol) and CuI (0.09 g, 0.49 mmol), were dissolved in 10 mL of THF under argon atmosphere then refluxed for 6 hr. (Scheme 2). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after separation dried with sodium sulfate. The solvent was removed under vacuum to give brown oily material with yield (1.1 g, 81%). HRMS= M^{+}_{calcd} for $C_{28}H_{47}N_3O_2Si = 485.34$. $(M+H)^{+}_{found} = 486.33$ and $(M+Na)^{+}_{found} = 508.32$ ($508.32 - 23 = 485.32$).

2.5. 1,3,5-trichloro-2,4,6-triiodobenzene (5).

Periodic acid (1.5 g, 6.55 mmol) was added slowly to 25 mL of concentrated sulfuric acid and stirred for one hour then Potassium iodide (3.25 g, 20 mmol) was added to the mixture slowly at 0 °C, after the reaction reached room temperature, 1,3,5-trichlorobenzene (**7**) (0.39 g, 2.2 mmol) was added (Scheme 3). The solution was poured into a mixture of ethyl acetate (25 mL) and water (25 mL). The organic layer after separation dried with sodium sulfate. The solvent was removed under vacuum to give solid materials with a yield (0.75 g, 62%), MP. 280 °C. HRMS= M^{+}_{calcd} for $C_3Cl_3I_3 = 557.62$. $(M+H)^{+}_{found} = 558.6$ and $(M+Na)^{+2}_{found} = 582.6$.

2.6. ((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tribenzene (6a)

1,3,5-trichloro-2,4,6-triiodobenzene (**5**) (0.5 g, 0.89 mmol), ethynylbenzene (0.27 g, 2.68 mmol), $Pd(PPh_3)_4$ (0.01 g, 0.09 mmol), CuI (0.03 g, 0.18 mmol) and Et_3N (0.28 g, 2.86 mmol) were dissolved in 10 mL of dioxane under argon atmosphere then stirred at 75 °C for 6 hr. (Scheme 3). The solution was poured into a mixture of ethyl acetate (10 mL) and water (10 mL). The organic layer after separation dried with sodium sulfate. Under vacuum the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to give white powder with yield (0.35 g, 81%), MP. 140-145 °C. 1H NMR (500 MHz, $CDCl_3$) (7.6 (m, 6H, Ar-H), 7.4 (m, 9H, Ar-H). ^{13}C NMR (126 MHz, $CDCl_3$) (142, 132.5, 129.2, 128.5, 121.8, 81.6, 74). HRMS= M^{+}_{calcd} for $C_{30}H_{15}Cl_3 = 481.80$. $(M+H)^{+}_{found} = 483.02$, and $(M+Na)^{+}_{found} = 505.0219$.

2.7. 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tripyridine (6b)

1,3,5-trichloro-2,4,6-triiodobenzene (**5**) (0.43 g, 0.76 mmol), 2-ethynylpyridine (0.24 g, 2.29 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.07 mmol), CuI (0.03 g, 0.15 mmol), Et_3N (0.24 g, 2.44 mmol) were dissolved in 10 mL of dioxane under argon atmosphere then stirred at 75 °C for 6 hr. (Scheme 3). The solution was poured into a mixture of ethyl acetate (10 mL) and water (10 mL). The organic layer after separation dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (3% EtOAc) as an eluent to give white powder with yield (0.29 g, 78%), MP. 195-200 °C. 1H NMR (500 MHz, $CDCl_3$) (7.45 (m, 3H), 7.42 (m, 6H), 7.3 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) (145.6, 140.8, 134, 133.8, 129.6, 128.69, 128.6, 100.4, 97.9). HRMS= M^{+}_{calcd} for $C_{27}H_{12}Cl_3N_3 = 483.02$. $(2M^{+})_{found} = 968.0178$.

2.8. 6,6',6''-((2,4,6-tris(phenylethynyl)benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine) (7a).

((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene (**6a**) (0.15 g, 0.31 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6((trimethylsilyl)ethynyl)-1,3,5-triazine (**3**) (0.48 g, 0.99 mmol), $Pd(PPh_3)_4$ (0.03 g, 0.03 mmol), CuI (0.01 g, 0.06 mmol) and K_2CO_3 (0.15 g, 1.08 mmol), were dissolved in 10 mL of dioxane under argon atmosphere then stirred at

80°C for 16 hours (Scheme 3). The solution was poured into a mixture of ethyl acetate (10 mL) and water (10 mL). The organic layer after separation dried with sodium sulfate. Under vacuum the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (2.5% EtOAc) as an eluent to give oily light brown material with yield (0.37 g, 74%). ¹H NMR (7.36 (m, 9H, Ar-H), 7.2 (m, 6H, Ar-H), 4.8 (s, 6H), 4.2 (t, 12H, OCH₂), 1.9 (m, 12H, CH₂), 1.74 (m, 18H, CH₃), 1.5-1.3 (m, 12H, CH₂), 1.1-0.88 (m, 36H, CH₂), 0.7 (m, 18H, CH₃). ¹³C NMR (126 MHz, CDCl₃) (172.5, 170.9, 133, 131.8, 129.7, 128.9, 125.1, 125.08, 122.3, 88.5, 86.45, 82, 74.4, 66.8, 42.8, 42.5, 37.7, 37.5, 36.4, 36.3, 30.22, 29.9, 29.4, 26.2, 25.9, 20.02, 19.9, 18.3, 13.7, 13.5, 13.25, 13.23). FT-IR (2969, 2919, 2853, 1748, 1566, 1525, 1495, 1460, 1431, 1410, 1303) cm⁻¹. HRMS = M⁺_{calcd} for C₁₀₅H₁₂₉N₉O₆ = 1612.01. (M+3H)⁺_{found} = 538.34 and (M+3Na)⁺_{found} = 560.67.

2.9. 6,6',6''-((2,4,6-tris(pyridin-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine) (7b).

2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tripyrindine (**6b**) (0.12 g, 0.25 mmol), Pd(PPh₃)₄ (0.03 g, 0.02 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**3**) (0.36 g, 0.74 mmol), CuI (0.01 g, 0.04 mmol) and K₂CO₃ (0.12 g, 0.86 mmol), were dissolve in in 10 mL of dioxane under argon atmosphere then stirred at 80 °C for 16 hours. (Scheme 3). The solution was poured into a mixture of ethyl acetate (10 mL) and water (10 mL). The organic layer after separation dried with sodium sulfate. Under vacuum, the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (2.5% EtOAc) as an eluent to give light brown with yield (0.25 g, 62%). ¹H NMR (500 MHz, CDCl₃) (7.58 (m, 3H, Ar-H), 7.4 (m, 3H, Ar-H), 7.22 (m, 6H, Ar-H), 4.9 (s, 6H), 4.23 (t, 12H, OCH₂), 1.84 (m, 18H, CH₂), 1.66 (m, 18H, CH₃), 1.5- 1.3 (m, 12H, CH₂), 1.25 – 0.86 (m, 36H, CH₂), 0.78 (m, 18H, CH₃). ¹³C NMR (171.7, 171.2, 142.5, 137.5, 136.2, 132.05, 131.14, 127.9, 124.7, 123.6, 121.9, 99.5, 99.3, 82, 67, 41.3, 41.1, 37.2, 35.9, 31.9, 29.6, 29.4, 25.7, 25.4, 22.62, 19.5, 17.6, 14.12, 13.5, 13.19). FT-IR (2966, 2925, 2853, 1732, 1566, 1521, 1501, 1458, 1430, 1411, 1374) cm⁻¹. HRMS: M⁺_{calcd} for C₁₀₂H₁₂₆N₁₂O₆ = 1616. (M+3Na)⁺_{found} = 561.98.

2.10. 4-(dodecyloxy) benzoic acid (4-DBA) (8)

4-hydroxy benzoic acid (8.2 mmol), 1-bromododecane (5.5 ml, 23 mmol, 2.8 eq) and KOH (1.3 g, 23 mmol, 2.8 eq) were dissolve in (25 ml) of ethanol and reflux for two days (Scheme 4). The mixture was hydrolysis by adding 10% aqueous KOH (12 ml) and refluxed overnight. After cooling down, the reaction mixture was acidified with HCl (6 M), the precipitate filtered, washed with water and recrystallized from ethanol to obtain the pure product 4-dodecyloxybenzoic acid white solid material with yield (4.55 g, 91 %). ¹H NMR (500 MHz, CDCl₃) (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). FT-IR (2914, 2848, 2559, 1670, 1604) cm⁻¹.

2.11. Synthesis of Organic Salts 9(a,b)

4-DBA mesogenic unit (**8**) reacted with **7(a-b)** in 10 mL of dry THF with one to one ratio (Scheme 4). The resulting solution was sonicated for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum.

The organic salt (9a). ¹H NMR (500 MHz, CDCl₃) (7.92 (d, 2H), 7.4 (d, 6H, Ar-H), 7.24 (m, 9H, Ar-H), 6.8 (d, 2H, Ar-H), 4.97 (s, 6H), 4.2 (t, 12H, OCH₂), 3.8 (t, 2H, OCH₂), 1.78 (t, 18H, CH₃), 1.6-1.3 (m, 24H, CH₂), 1.1- 0.9 (m, 60H, CH₂), 0.78 (m, 18H, CH₃). ¹³C NMR (171.7, 170, 165, 163, 132.5, 132.3, 131.3, 131.2, 129, 128, 124, 121.7, 121.3, 114.18, 81.5, 73.8, 68, 66, 42, 41.2, 37.3, 35.6, 32.4, 30.2, 31, 29.9, 29.8, 29.5, 28.8, 26.3, 25.8, 23.3, 22, 19.8, 18.1, 17, 14.6, 12). FT-IR (2916, 2846, 1674, 1603, 1522, 1503, 1459, 1425, 1362, 1335). HRMS= M⁺_{calcd} for C₁₂₄H₁₅₉N₉O₉ = 1918.23. (M + 3K)⁺_{found} = 678.7.

The organic salt (9b). ¹H NMR (500 MHz, CDCl₃) (7.9 (d, 2H, Ar-H), 7.58 (m, 6H), 7.4 (m, 3H), 7.22 (m, 3H), 6.75 (d, 2H, Ar-H), 4.9 (s, 6H), 4.2 (t, 12H, OCH₂), 3.75 (t, 2H, OCH₂), 1.78 (t, 18H, CH₃), 1.6-1.3 (m, 24H, CH₂), 1.1- 0.9 (m, 60H, CH₂), 0.78 (m, 18H, CH₃). FT-IR (2923, 2852, 1736, 1567, 1521, 1501, 1458, 1413). HRMS = M⁺_{calcd} for C₁₂₁H₁₅₆N₁₂O₉ = 1921.21. (M+3K)⁺_{found} = 680.36 and 679.7.

3. RESULTS AND DISCUSSION:

In this study, six-armed compounds based on benzene ring as a central core was synthesized via sonogashira reaction. 1,3,5-trichlorobenzene and 2,4,6-trichloro-1,3,5-triazine were the starting material. The intermediate compound 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-

triazine was obtained by sequential nucleophilic substitution of chlorine atoms in cyanuric chloride and used further in the synthesis of six armed structures as described in (Scheme 2 - 4). The obtained compounds were confirmed by spectroscopic analysis and the organic salts were investigated by polarized optical microscope (POM) and differential scanning calorimetry (DSC).

The formation of ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm^{-1} shifted to 1566 cm^{-1} in both organic salt (**9a**, **9b**). Whereas, the stretching vibration of the C=C bond in both organic salt appears at 1675 cm^{-1} and 1635 cm^{-1} (Figure 1). Besides, peaks at 2900 and 2800 cm^{-1} belonging to hydrogen stretching (Türkçü, 2016).

Also, NMR spectroscopy confirmed the formation of organic salt (**9a**, **9b**). The signals belong to the aromatic protons of alkoxy benzoate unit in both compounds shift to (7.8, 6.7) ppm and (7.9, 6.75) ppm respectively as compared with the signals of pure 4-DBA at (8.05, 6.95) ppm, due to increase in electron density of aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field 3.8 ppm and 3.75 ppm as compared with the signals of pure 4-DBA at 4.05 ppm (Figure 2). Additionally, the singlets of aromatic ring protons in organic salt (**9a**, **9b**) didn't show any shifting due to their electronic environment did not change. These changes in chemical shift related to the difference in electron density after the interaction.

However, the ^{13}C NMR spectra show that the carbonyl carbon of 4-DBA shifted from 171.6 to 165.12 ppm, similarity the aromatic carbon next to alkoxy group of 4-DBA shift slightly from 163.69 to 163.6 ppm. These change in chemical shift due to decrease of electron density after the ionic interaction (Figure 3). Additionally, the peaks which belong to triazine ring didn't show any shifting.

Additionally, the mass spectrometry of organic salt (**9a**) confirmed the molecular structure by the presence of $(M+3K)^{+3}$ at 678.70 peaks, which correspond to $\text{C}_{124}\text{H}_{159}\text{N}_9\text{O}_9$, similarity the molecular structure of organic salt (**9b**) confirmed by the presence of $(M+3K)^{+3}$ peaks at 680.36 and 680.03, which correspond to $\text{C}_{121}\text{H}_{156}\text{N}_{12}\text{O}_9$, (Figure 4).

Compound 4-DBA, which has a terminal chain, and already shows liquid crystalline, so to obtain liquid crystalline material for our synthesized compounds, the equimolar mixture between six-

armed π -conjugated system and 4-DBA was obtained through ionic interaction. Concerning to 4-DBA, upon heating showed three peaks corresponding to Cr-SmC-N-Iso transitions. On cooling from 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°C was detected in cooling DSC thermogram (Kumar, 2010; Pisupati, 2000).

The equimolar mixtures of the organic salt (**9a**, **9b**) based on the benzene core were investigated by using an optical polarizing microscope (PM) and differential scanning calorimeter (DSC). The compounds (**9a**, **9b**) show one endotherm corresponds to crystal to the isotropic (Iso) transition in heating DSC thermogram. The organic salts (**9a**, **9b**) show no liquid crystal behavior by an optical polarizing microscope (PM) observation.

The organic salt (**9a**, **9b**) exhibit a phase transition sequence of Cr-Col-Iso, which is in agreement with two endotherms in DSC heating curves. Compound (**9a**) on cooling from the isotropic liquid, exhibited one peak in phase transition with the dendritic growing texture was observed between $(64-18)^\circ\text{C}$, whereas compound (**9b**) phase transition with the growing dendritic texture was observed between $(71-20)^\circ\text{C}$, (Figure 5). Both organic salts with multi-side chains, the differential scanning calorimetry, and optical polarized microscope showed no liquid crystal behavior.

4. CONCLUSIONS:

New six arms macromolecular structures was efficiently prepared which composed of 1,3,5-trichlorobenzene central core, three armed of 2-Ethynylpyridine (2-Ethynylbenzene), and three armed of 1,3,5-triazine rings carrying dodecyloxy chains which are positioned at the peripheries of the central core by acetylenic bridges. The six-armed compounds was non liquid crystal therefore the compounds were mixed with 4-dodecyloxy benzoic acid to obtain organic salt. The organic salts, which made between the π -conjugated system and 4-dodecyloxy benzoic acid were investigated for their liquid crystal properties by optical polarizing microscope (POM) and differential scanning calorimetry (DSC), it's found no liquid crystalline behaviours even after ionic interaction through hydrogen bonding. All the synthesized compounds were confirmed by spectroscopic analyses (^{13}C NMR, ^1H NMR, FT-IR, and HRMS).

5. REFERENCES:

- Bremer M, Kirsch P, Klasen-Memmer M, Tarumi K. (2013). The TV in your pocket: Development of liquid-crystal materials for the new millennium. *Angewandte Chemie* (International Ed. in English). 52(34):8880-8896. DOI: 10.1002/anie.201300903
- Kato T, Uchida J, Ichikawa T, Sakamoto T. (2018). Functional liquid crystals towards the next generation of materials. *Angewandte Chemie* (International Ed. in English). 57(16):4355-4371. DOI: 10.1002/anie.201711163
- Scutaru, D., Carlescu, I., Bulai, E. R., Ciobanu, C. I., Lisa, G., and Hurdac, N. (2018). Bent-Core Liquid Crystals: Structures and Mesomorphic Properties. *Liquid Crystals-Self-Organized Soft Functional Materials For Advanced Applications*.
- Akkurt, N., Al-Jumaili, M. H. A., ERAN, B. B., Ocak, H., and Torun, L. (2019). Acetylene-bridged triazine π -conjugated structures: synthesis and liquid crystalline properties. *Turkish Journal of Chemistry*, 43(5), 1436-1444.
- Praefcke, K., Kohne, B., Gündogan, B., Singer, D., Demus, D., Diele, S., ... and Bakowsky, U. (1991). News on nematic-biaxial liquid crystals. *Molecular Crystals and Liquid Crystals*, 198(1), 393-405.
- Al-Jumaili, M. H., Hamed, A. S., Akkurt, N., and Torun, L. (2020) Six-armed Structures Based on Benzene Ring, Synthesis and Characterization Via Sonogashira Coupling. *Indonesian Journal of Chemistry*.
- Kondo, K., Yasuda, S., Sakaguchi, T., and Miya, M. (1995). The third-order optical non-linearity of the phenylethynyl-substituted benzene system. *Journal of the Chemical Society, Chemical Communications*, (1), 55-56.
- Kayser, B., Altman, J., and Beck, W. (1999). Benzene-Bridged Hexaalkynylphenylalanines and First-Generation Dendrimers Thereof. *Chemistry-A European Journal*, 5(2), 754-758.
- Mongin, O., Hoyler, N., and Gossauer, A. (2000). Synthesis and Light-Harvesting Properties of Naphthyrins. *European Journal of Organic Chemistry*, 2000(7), 1193-1197.
- Kehoe, J. M., Kiley, J. H., English, J. J., Johnson, C. A., Petersen, R. C., and Haley, M. M. (2000). Carbon networks based on dehydrobenzoannulenes. 3. synthesis of graphyne substructures. *Organic letters*, 2(7), 969-972.
- Wan, W. B., Brand, S. C., Pak, J. J., and Haley, M. M. (2000). Synthesis of expanded graphdiyne substructures. *Chemistry-A European Journal*, 6(11), 2044-2052.
- Sonoda, M., Inaba, A., Itahashi, K., and Tobe, Y. (2001). Synthesis of differentially substituted hexaethynylbenzenes based on tandem Sonogashira and Negishi cross-coupling reactions. *Organic letters*, 3(15), 2419-2421.
- Boger, D. L., Schaum, R. P., and Garbaccio, R. M. (1998). Regioselective Inverse Electron Demand Diels-Alder Reactions of N-Acyl 6-Amino-3-(methylthio)-1, 2, 4, 5-tetrazines. *The Journal of organic chemistry*, 63(18), 6329-6337.
- Sakya, S. M., Groskopf, K. K., and Boger, D. L. (1997). Preparation and inverse electron demand Diels-Alder reactions of 3-methoxy-6-methylthio-1, 2, 4, 5-tetrazine. *Tetrahedron letters*, 38(22), 3805-3808.
- Novák, Z., and Kotschy, A. (2003). First cross-coupling reactions on tetrazines. *Organic letters*, 5(19), 3495-3497.
- Chow, T. J. (Ed.). (2014). *Organic structures design: applications in optical and electronic devices*. CRC Press.
- Tan, Z. Y., Wu, K. X., Huang, L. S., Wu, R. S., Du, Z. Y., and Xu, D. Z. (2020). Iron-catalyzed cross-dehydrogenative coupling of indolin-2-ones with active methylenes for direct carbon-carbon double bond formation. *Green Chemistry*.
- Usta, H., Sheets, W. C., Denti, M., Generali, G., Capelli, R., Lu, S., ... and Facchetti, A. (2014). Perfluoroalkyl-functionalized thiazole-thiophene oligomers as n-channel semiconductors in organic field-effect and light-emitting transistors. *Chemistry of Materials*, 26(22), 6542-6556.
- Kaller, M., Beardsworth, S. J., Staffeld, P., Tussetschlager, S., Gießelmann, F., and Laschat, S. (2012). Increased mesophase range in liquid crystalline crown ethers via lower molecular symmetry. *Liquid Crystals*, 39(5), 607-618.
- Kumar, S. (2005). Triphenylene-based discotic liquid crystal dimers, oligomers and polymers. *Liquid crystals*, 32(9), 1089-1113.

21. Kestemont, G., De Halleux, V., Lehmann, M., Ivanov, D. A., Watson, M., and Geerts, Y. H. (2001). Discotic mesogens with potential electron carrier properties. *Chemical communications*, (20), 2074-2075.
22. Gsänger, M., Oh, J. H., Könnemann, M., Höffken, H. W., Krause, A. M., Bao, Z., and Würthner, F. (2010). A crystal-engineered hydrogen-bonded octachloroperylene diimide with a twisted core: an n-channel organic semiconductor. *Angewandte Chemie International Edition*, 49(4), 740-743.
23. Sergeyev, S., Pisula, W., and Geerts, Y. H. (2007). Discotic liquid crystals: a new generation of organic semiconductors. *Chemical Society Reviews*, 36(12), 1902-1929.
24. Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., and Vill, V. (Eds.). (2011). *Handbook of liquid crystals, volume 2A: low molecular weight liquid crystals I: calamitic liquid crystals*. John Wiley and Sons.
25. Lehmann, M. (2009). Star Mesogens (Hekates)—Tailor-Made Molecules for Programming Supramolecular Functionality. *Chemistry—A European Journal*, 15(15), 3638-3651.
26. Pradhan, B., Pathak, S. K., Gupta, R. K., Gupta, M., Pal, S. K., and Achalkumar, A. S. (2016). Star-shaped fluorescent liquid crystals derived from s-triazine and 1, 3, 4-oxadiazole moieties. *Journal of Materials Chemistry C*, 4(25), 6117-6130.
27. Bisoyi, H. K., and Kumar, S. (2010). Discotic nematic liquid crystals: science and technology. *Chemical Society Reviews*, 39(1), 264-285.
28. Kumar, C. R. S., Jha, A., and Sastry, S. S. (2010). Induced crystal G phase of liquid crystalline amide through inter molecular hydrogen bonding. *Journal of non-crystalline solids*, 356(6-8), 334-339.
29. Pisupati, S., Kumar, P. A., and Pisupati, V. G. K. M. (2000). Induced crystal G phase through intermolecular hydrogen bonding II. Influence of alkyl chain length of n-alkyl p-hydroxybenzoates on thermal and phase behaviour. *Liquid Crystals*, 27(5), 665-669.
30. Türkçü, H. N., Ocağ, H., Gürbüz, M. U., Çakar, F., Bilgin-Eran, B., and Tülü, M. (2016). A study of dendritic ionic liquid crystals: Using (S)-4-citronellyloxybenzoic acid and polypropylene imine dendrimers. *Journal of Molecular Liquids*, 216, 209-215.

Scheme 2. Synthesis of intermediate compound

Reaction and conditions: i) 3,7-dimethyloct-6-en-1-ol (2 eq), K_2CO_3 , 0-50°C, 6hr, THF, ii) Trimethylsilyl acetylene, K_2CO_3 , Pd (PPh_3)₄, CuI, THF, Reflux.

Scheme 3. Synthesis of six-armed compounds

Reaction and condition: i) 2-Ethynylpyridine (2-Ethynylbenzene), Pd(PPh_3)₄ (0.02), CuI (0.04), Et_3N (3.2 eq), Dioxane, 75 °C, 6 hr. ii) Pd(PPh_3)₄, CuI, K_2CO_3 , Dioxane, 80°C, 16 hr.

Scheme 4: Synthesis procedure of organic salt (9a, 9b).

Figure 1. FT-IR spectra of organic salts (9a, 9b) and benzoic acid (4-DBA).

Figure 2. The comparison of ^1H NMR spectra (in CDCl_3) of organic salts (9a, 9b) and benzoic acid (4-DBA).

Figure 3. ^{13}C NMR spectra (in CDCl_3) of compound (7a), organic salt (9a) and benzoic acid (4-DBA).

Figure 4. HRMS result of organic salt (9a, 9b).

Figure 5. Optical textures of organic salt (9a (left), 9b (right)) as observed between crossed polarizers in an ordinary glassplates. C) A typical texture of smectic C mesophase of compound 4-DBA.

Table 1. Mesophases and phase transition temperatures as observed on heating (H→) and cooling (←C) and corresponding transition enthalpies of organic salts (9a, 9b) 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 (9a)	H → : Cr 52 [170.46], Col 81.53 [22.4] Iso Cr 16.30 [142.59] Col 69 [11.2] Iso : ← C
OS (9b)	H → : Cr 25.2 [190.46], Col 78.4 [19.4] Iso Cr 18.2 [182.73] Col 64 [13.2] 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.