

Synthesis, Characterization And Liquid Crystalline Properties Of (E)-4-((4-(Alkanoylthio)Phenyl)Diazenyl) Benzoic Acid

Ekhlas Aziz Bakr and Abdullah Hussein Kshash

Abstract: In this study, a series of azo thioester consisting of 9 compounds were synthesized by using (E)-4-((4-mercaptophenyl)diazenyl)benzoic acid as backbone of compounds. These compounds were synthesized by diazotization of 4-aminobenzoic acid then coupling with thiophenol, followed by acylation of thiol group with acid chloride (2-10 carbon atoms) in pyridine as a solvent. Synthesized compounds were characterized by using IR, ¹H NMR spectroscopy, their melting points were determined, investigation of liquid crystalline properties indicated that no liquid crystal properties for these compounds.

Index Terms: Azo, Thioester, diazotization, thiophenol, liquid crystal

1. INTRODUCTION

Liquid crystal (LC) is intermediate state of matter produced by special ordering in between of solid and liquid state. There are wide applications of LC as textile industry, medical thermographic instruments, photoconductors and semiconductor materials and pharmaceutical preparations because they show isotropic nature such as fluid and crystal nature such as solid [1-3]. There are two common types of liquid crystals thermotropic and lyotropic [4]. Thermotropic LC properties depend on a change of temperature [5], while lyotropic LC depends on a change in concentration. Liquid crystalline materials are very important for material sciences and life sciences. The novel design of thermotropic liquid crystals are considered as advanced functional materials that include the suitable selection of core fragment of linking group as azo [6,7] ester [8] chalcon [9] and azomethine [10] and terminal functionality. The mesomorphic behavior of mesogens relies on the molecular structure of molecules and molecular forces arising, and hence, a little change in the molecular geometry brings about significant change in its mesomorphic properties. Lateral substitution makes the molecule broad and hence plays a very important function in the mesogenic properties of the materials that could be utilized proficiently for applications,[11]. This study has been directly focused on the synthesization of a novel homologous series containing of azo central linkages that show liquid crystalline properties of compounds substantial because of presence of trans-cis photochemical isomerization of the azobenzene moiety [12,15]. Azo central linkages have also been intensively investigated in last year's due to the novel properties of the azo when linked with other groups and they have own potential applications in the field of optical [16,17]. Moreover, number of mesogenic homologous series of thioester with carboxylic acid group terminal has been synthesized as shown in Figure 1. The terminal substituents play an important role in promoting liquid crystalline properties in a mesogen with high thermal stability [18,19]. on the other side, the appearance of a

mesogenic compound have been known to promote or suppress its mesomorphic properties dependent on substituents with different polarities residing at both terminals along the molecular axis of a mesogenic compound. From the model terminal substituents, such as COOH and thioester as polar groups possessing dipole moments which support mesomorphic properties, the increased dipole moment enhances the stability of lattice and therefore increases its melting temperatures, [20,21]. In addition, it is noticed in the previous research, azo compounds have been very remarkable in many miscellaneous application areas like chorography, displays, optical storage devices, photonics to medicine, photo chemical molecular switches [22-27].

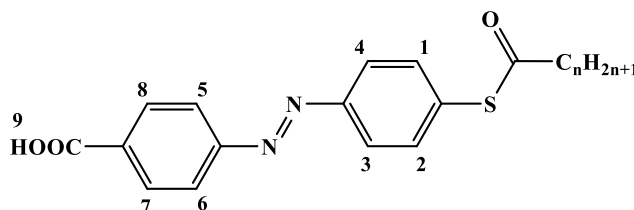


Fig. 1. Molecular structure of desired azo thioester derivatives.

2 EXPERIMENTAL SECTION

2.1 Materials and Instrumentation

Infrared spectra were recorded as ATR technique on Bruker-Tensor 27 spectrometer. ¹H-NMR and recorded on Bruker-300 MHz spectrometer using DMSO-d₆ as a solvent and TMS (tetramethylsilane (CH₃)₄Si) as internal standard., TLC eluent (heptane:ethanol) (9:1) and developed by iodine, Chemical were supplied from Sigma-Aldrich Co. used directly without further purification, solvents were supplied from Scharlau.

2.2. Synthesis

(E)-4-((4-mercaptophenyl)diazenyl)benzoic acid.

4-amino benzoic acid (0.01 mol), were dissolved in 50 mL of distilled water contained in 100 mL, 8 mL of HCl acid was added. The mixture was kept in ice bath at 0 - 5°C. Then 10 mL solution of 0.011 mole of NaNO₂ was added drop wise for

- Ekhlas Aziz Bakr: Department of Chemistry - College of education for pure Science – University of Anbar
- Abdullah Hussein Kshashi' Department of Chemistry - College of education for pure Science – University of Anbar (email: drabdullahkshash@gmail.com)

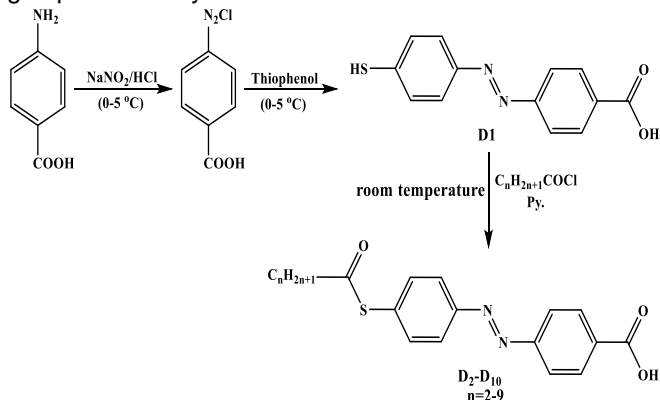
30 minutes. 20 mL solution of 0.01 mole of NaOH and 0.01 mole thiophenol in 15 mL distilled water were added, reaction mixture was stirred for 2 hr. precipitate was filtered and washed with distilled water.

[D1]: (E)-4-((4-mercaptophenyl)diazenyl)

benzoic acid: Deep yellow solid, yield 85 %; mp 120-122 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}), 3048 (C-H_{aromatic}), 2662 (v S-H), 1679 (C=O_{Carboxylic acid}), 1420 (v N=N), ¹H NMR: (300 MHz, DMSO-d₆) δ 3.35 (s, 1H, S-H), 7.80-7.82 (d, 2H, H_{1,2}), 7.86 – 7.88 (d, 2H, H_{3,4}) for H_{3,4}, 7.94-7.96 (d, 2H, H_{5,6}), 8.10-8.13 (d, 2H, H_{7,8}), and 13.02 (s, 1H, H₉).

2.2.1. Synthesis of compounds (2-9)

Objective compounds were synthesized as described in scheme 1, by main three steps includes: preparation of 4-(chloro diazenyl)benzoic acid as diazonium salt using 4-amino benzoic acid as aromatic primary amine, then coupling of thiophenol with diazonium salt in basic medium, finally synthesis of 4-((4-(alkanoylthio)phenyl)diazenyl) Benzoic Acid (which is the backbone for target molecules) by reaction of carboxylic acid chloride with thiol group via tetrahedral mechanism, electron per of sulfur atom attack on the carbonyl group for carboxylic acid chloride as shown in1.



Scheme1.Synthetic route for (E)-4-((4-(alkanoylthio)phenyl)diazenyl) Benzoic Acid.

[D2]: (E)-4-((4-(acetylthio)phenyl)diazenyl)

benzoic acid:

Pale yellow solid, yield 96 %; MP158-160 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3050 (Ar-H), 2976 (v C-H_{aliphatic}), 1718 (C=O_{Carboxylic acid}), 1781(C=O_{thioester}), 1431 (v N=N), ¹H NMR: (300 MHz,) δ 7.80-7.82 (d, 2H, H_{1,2}), 7.86 – 7.88 (d, 2H, H_{3,4}), 7.95-7.97 (d, 2H, H_{5,6}), 8.10-8.13 (d, 2H, H_{7,8}), and 13.09 (s, 1H, H₉).

[D3]:(E)-4-((4-(propionylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 78 %; MP 148-150 °C, IR (ATR) cm^{-1} 2500-3350 (O-H_{carboxylic acid}) 3051 (Ar-H), 2987 (v C-H_{aliphatic}), 1718 (C=O_{Carboxylic acid}), 1781(C=O_{thioester}), 1438 (v N=N), ¹H NMR: (300 MHz,) δ 7.80-7.82 (d, 2H, H_{1,2}), 7.86 – 7.88 (d, 2H, H_{3,4}), 7.94-7.96 (d, 2H, H_{5,6}) 8.10-8.12 (d, 2H, H_{7,8}), and 13.06 (s, 1H, H₉).

[D4]: (E)-4-((4-(butyrylthio)phenyl)diazenyl)benzoic acid:

Pale yellow solid, yield 80 %; MP. 133-135 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3050 (Ar-H), 2972 (v C-H_{aliphatic}), 1717 (C=O_{Carboxylic acid}), 1781(C=O_{thioester}), 1439 (v N=N), ¹H NMR: (300 MHz,) δ 7.80-7.82 (d, 2H, H_{1,2}), 7.85 – 7.88 (d, 2H, H_{3,4}), 7.94-7.96 (d, 2H, H_{5,6}), 8.10-8.12 (d, 2H, H_{7,8}), and 13.00 (s, 1H, H₉).

[D5]: (E)-4-((4-(pentanoylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 75 %; MP 128-130 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3053 (Ar-H), 2986 (v C-H_{aliphatic}), 1698 (C=O_{Carboxylic acid}), 1679(C=O_{thioester}), 1418 (v N=N), ¹H NMR: (300 MHz,) δ 7.58-7.60 (d, 2H, H_{1,2}), 7.64 – 7.66 (d, 2H, H_{3,4}), 7.77-7.79 (d, 2H, H_{5,6}), 8.05-8.07 (d, 2H, H_{7,8}) and 13.13 (s, 1H, H₉).

[D6]: (E)-4-((4-(hexanoylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 74 %; MP 113-115 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3051 (C-H_{aromatic}), 2987 (v C-H_{aliphatic}), 1718 (C=O_{Carboxylic acid}), 1782 (C=O_{thioester}), 1431 (v N=N), ¹H NMR: (300 MHz,) δ 7.80-7.82 (d, 2H, H_{1,2}), 7.86 – 7.88 (d, 2H, H_{3,4}), 7.94-7.96 (d, 2H, H_{5,6}), 8.10-8.12 (d, 2H, H_{7,8}), and 13.09 (s, 1H, H₉).

[D7]: (E)-4-((4-(heptanoylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 66 %; MP 108-110 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3060 (Ar-H), 2954 (v C-H_{aliphatic}), 1678 (C=O_{Carboxylic acid}), 1699 (C=O_{thioester}), 1419 (v N=N), ¹H NMR: (300 MHz,) δ 7.24-7.26 (d, 2H, H_{1,2}), 7.36 – 7.38 (d, 2H, H_{3,4}), 7.86-7.88 (d, 2H, H_{5,6}), 7.96-7.97 (d, 2H, H_{7,8}) and 12.78 (s, 1H, H₉).

[D8]:(E)-4-((4-(octanoylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 65 %; MP 120-122 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3052 (Ar-H), 2955 (v C-H_{aliphatic}), 1678 (C=O_{Carboxylic acid}), 1782 (C=O_{thioester}), 1419 (v N=N), ¹H NMR: (300 MHz,) δ 7.24-7.26 (d, 2H, H_{1,2}), 7.37 – 7.39 (d, 2H, H_{3,4}), 7.50-7.52 (d, 2H, H_{5,6}), 7.86-7.88 (d, 2H, H_{7,8}) and 12.68 (s, 1H, H₉).

[D9]:(E)-4-((4-(nonanoylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 67 %; MP 120-122 °C, IR (ATR) cm^{-1} 2500-3350 (O-H_{carboxylic acid}) 3049 (Ar-H), 2954 (v C-H_{aliphatic}), 1678 (C=O_{Carboxylic acid}), 1698 (C=O_{thioester}), 1419 (v N=N), ¹H NMR: (300 MHz,) δ 7.36-7.38 (d, 2H, H_{1,2}), 7.50 – 7.52 (d, 2H, H_{3,4}), 7.86-7.88 (d, 2H, H_{5,6}), 7.95-7.97 (d, 2H, H_{7,8}) and 12.56 (s, 1H, H₉).

[D10]: (E)-4-((4-(decanoylthio)phenyl)diazenyl)benzoic acid: Pale yellow solid, yield 67 %; MP 128-130 °C, IR (ATR) cm^{-1} 2500- 3350 (O-H_{carboxylic acid}) 3051 (Ar-H), 2987 (v C-H_{aliphatic}), 1717 (C=O_{Carboxylic acid}), 1782 (C=O_{thioester}), 1431 (v N=N), ¹H NMR: (300 MHz,) δ 7.80-7.82 (d, 2H, H_{1,2}), 7.86 – 7.88 (d, 2H, H_{3,4}), 7.94-7.96 (d, 2H, H_{5,6}), 8.10-8.12 (d, 2H, H_{7,8}), and 12.99 (s, 1H, H₉).

3. SPECTRAL DATA FTIR AND ¹H NMR

The formation of (E)-4-((4-mercapto phenyl)diazenyl)benzoic acid (D₁) was confirmed by FT-IR spectrum, the corresponding signal of carboxylic acid group observed as a broad band at 3350- 2500 cm^{-1} , whereas the signal at 2662 cm^{-1} related to v S-H, besides, the carbonyl group (C=O) signal observed at 1679 cm^{-1} , also the signal of azo group observed at 1420 cm^{-1} . The formation of compound D₁ was also confirmed by ¹H-NMR spectrum. The corresponding peak of S-H appears at 3.35 ppm. However, the aromatic hydrogen peaks observed at 7.82-7.80 ppm (H_{1,2}), 7.88 – 7.86 ppm (H_{3,4}), 7.96-7.94 ppm (H_{5,6}), 8.13-8.10 ppm (H_{7,8}), Besides, the carboxylic hydrogen appears at 13.02 ppm as a singlet. FT IR spectra indicate the obtained of (D₂-D₁₀) compounds by appearance of thioester band at range 1678-1718 cm^{-1} , and disappeared thiol band, whereas aliphatic proton observed at 2987-2954, which belongs to alkyl chain for thioester, other results for IR spectra are given in Table 1.

Table1. FTIR spectral data (cm⁻¹) for synthesized D₂-D₁₀ compound.

comp	ν C-H		ν C=O		ν C=C	ν N=N
	Arom.	Aliph	este thio	carbo xyl		
D ₂	3050	2976	1781	1718	1600	1431
D ₃	3051	2987	1781	1718	1600	1578
D ₄	3050	2972	1781	1717	1600	1578
D ₅	3053	2986	1679	1698	1575	1497
D ₆	3051	2987	1782	1718	1600	1579
D ₇	3060	2954	1678	1699	1600	1577
D ₈	3052	2955	1782	1678	1598	1577
D ₉	3049	2954	1678	1698	1598	1577
D ₁₀	3051	2987	1782	1717	1600	1579

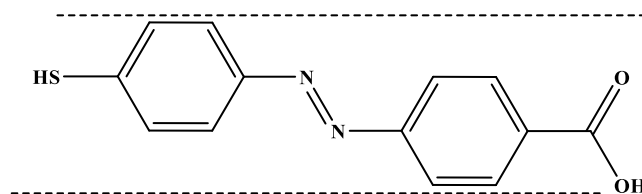
The formation of our compounds was mainly confirmed by ¹H-NMR and FT-IR. ¹H-NMR indicates disappearance of the signal of the thiol group (D₂-D₁₀) compounds at 3.35 ppm and appearance of variable signals for aliphatic protons at range 2.53-0.86 ppm depending on hydrocarbon chain length, while the aromatic ring protons observed at range 8.18-7.10 ppm, Fig. 4 NMR spectra for D₂ compound. ¹H-NMR spectral data are given in Table 2.

Table2. NMR spectral data (ppm) for synthesized D₂-D₁₀ compound.

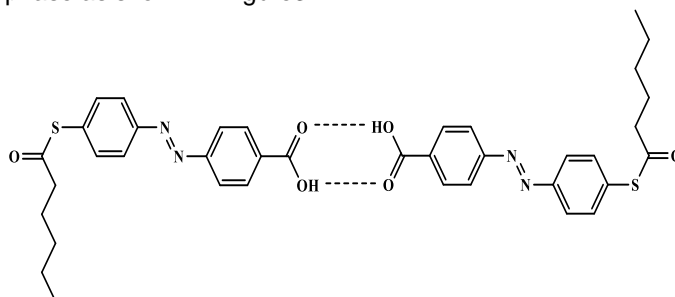
Comp.	CH ₃	CH ₂	βCH ₂	αCH ₂	Ar-H	COOH
D ₂	2.34s	-	-	-	7.77 - 8.18 m	13.09 s
D ₃	1.08 t	-	-	2.5 3t	7.80 - 8.15 m	13.06 s
D ₄	0.98 t	-	1.23 m	2.4 1t	7.80 - 8.13 m	13.00 s
D ₅	0.85 t	124 m	1.40 p	2.4 5t	7.57 - 8.08 m	13.13 s
D ₆	0.86 t	0.87 m	1.06 p	2.3 3t	7.79 - 8.13 m	13.09 s
D ₇	0.89 t	1.14 - 1.31m	1.52 p	2.0 5t	7.22 - 7.97 m	12.78 s
D ₈	0.86 t	1.24 -152 m	1.64 p	2.2 0t	7.20 - 7.88 m	12.68 s
D ₉	0.86 t	1.15 - 1.31 m	1.152 p	2.2 0t	7.35 - 7.89 m	12.56 s
D ₁₀	0.87 t	1.24 - 1.48m	1.57 p	2.2 1t	7.77 - 8.13 m	12.99 s

4. RESULT AND DISCUSSION:

In current research, a homologues series of (E)-4-((4-mercapto phenyl)diazenyl)benzoic acid were synthesized efficiently and confirmed by spectroscopic techniques. Their mesomorphic properties were studied by polarized optical microscopy and differential scanning calorimetry. Our result indicated that no liquid crystal properties for these compounds due to the backbone of (E)-4-((4-mercaptophenyl)diazenyl)benzoic acid (D₁) which is linear as the conjugation of aromatic rings by azo group as shown in Figure3.

**Fig.2.** Linearity of (D₁) Compound.

The non-liquid crystalline properties of these compounds could be related to the low electronegativity, larger sulfur atom size and carbonyl group pushing the chain down the molecule. Besides, hydrogen bonding between molecules (dimer molecule) increases the molecular width. All these reasons led to irregularity of the molecules to give the required crystalline phase as shown in Figure3.

**Fig.3.** dimer molecule for synthesized compound.

5. CONCLUSION

We have successfully synthesized and characterized homologous series with central azo and thioester carboxylic acid group, terminal substituents which were proved by FT-IR and ¹H-NMR spectroscopy, while the study of liquid crystals properties by POM and DSC indicates that no liquid crystal behavior for synthesized compounds.

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