

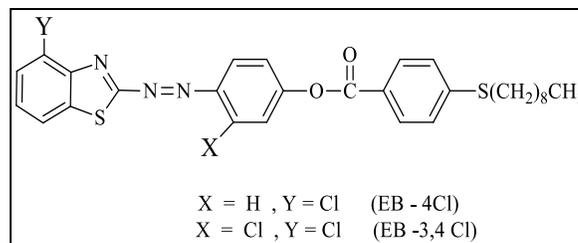
Synthesis and characterization of AZO-Benzothiazole compounds and study the effect of lateral substituents on their liquid crystalline properties supported by the theoretical results.Afrah Abdul-Radha'e Mahdi Aljaber^{1*}, Ayat Asaad Fadhl Alali², Saja Abdul-Hussein Talib Al-shalashat³¹ Department of Chemistry, Ministry of Education, Basrah Education, Basrah, Iraq² Department of Chemistry, College of Education, Basrah University, Basrah, Iraq³ Department of Chemistry and Petroleum Engineering, College of Engineering, Al-Maaqal University, Basrah, IraqDOI: <https://doi.org/10.33545/26646552.2021.v3.i1.a.20>**Abstract**

Compounds EB-4Cl and EB-3,4Cl were prepared and diagnosed by spectral methods FTIR, NMR and Mass. They also studied by polarized microscope and did not diagnose any liquid crystalline phases in the compounds. The total dipole moment of the molecules and the length and width of the molecules as well as the length of the bonds were theoretically calculated.

Keywords: azo; lateral group; benzothiazole, liquid crystal**Introduction**

Thermotropic Liquid Crystals molecules normally consist of aromatic molecular core connected by different linking groups, e.g. azomethine ($-C=N-$), azo ($-N=N-$) and ester ($-COO-$). The choice of linking groups in Liquid Crystals compounds is very crucial because a linking group can increase the overall molecular length and the polarizable anisotropy of mesogen and hence may provide favorable geometry of the molecule^[1]. For example azo and ester linking groups in the mesogenic core could allow achieving an anticipated mesophase as well as multifunctional materials with improved properties. In this connection, a large number of research groups have been working with azo-ester linking LC materials with an aim to study the effect of varying alkyl chain length, lateral substituents and terminal group on the thermal and mesomorphic behaviors^[2-6].

It may be thought that anything that sticks out at the side of a molecule obviously disrupts molecular packing and therefore reduces liquid crystal phase stability. Indeed such disruption nearly always occurs through lateral substitution, but the situation is very subtle. In many cases this disruption to the molecular packing is particularly advantageous for the mesomorphic and physical properties required for applications, and some very interesting and useful materials have been generated by the appropriate use of lateral substitution^[7]. For many years it was believed that a lateral substituent on the rigid core of a liquid crystal depress the Nematic-isotropic transition temperature according to the size of the substituent irrespective of its other properties such as polarizability and polarity. Hence, it was assumed that only relatively small lateral substituents may be incorporated into a mesogenic structure without destruction of liquid-crystalline behavior^[8]. In this article, we describe the synthesis, characterization, thermal mesophase, properties of two azo-benzothiazole moiety based LC materials with lateral group:

**Fig 1****Experimental****General**

Infrared spectra were recorded as KBr pellets on a Buck - M500 spectrometer (Buck Scientific, USA). ¹H-NMR spectra were recorded on a Gemini - 200 instrument using CDCl₃ and DMSO as solvent and TMS as internal standard (Varian, Germany). Elemental analysis was performed on a Euro Vector (Italy) EA 3000A instrument. The phase transitions were observed with a LeitzL aborlux 12 Pol optical microscope with polarized light in conjunction with a Leitz 350 hot stage (Germany) equipped with a Vario - Orthomat. Transition temperatures were determined using a Shimadzu 24 DSC-50 differential scanning calorimeter (Japan) with a heating rate of 10 °C min⁻¹.

Synthesis of azo compounds**A. Diazotization of anilines**

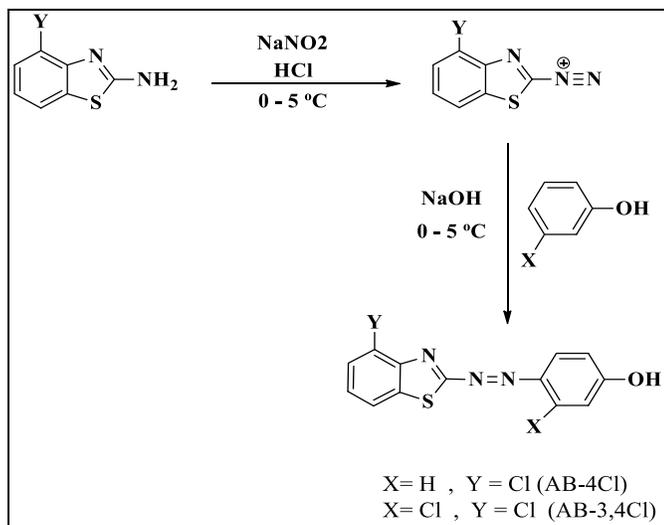
A solution of 2-(4-Amino) benzothiazol (10 mmol) and 3M HCl (8 mL) was heated gently, then water (10 mL) was added in order to dissolve the solid.

The mixture was cooled to 0 °C in an ice bath with stirring. Some solid may precipitate, but the reaction will still work well if it is stirred. Freshly prepared 1M sodium nitrite solution (10 mL) was then added slowly with stirring. The rate of addition was adjusted so that the temperature of the solutions remains below 10 °C. The

solution was kept in an ice bath and used immediately in the next step [9].

B. Coupling with phenols

A solution of one of the substituted phenols (10 mmol) in 1M NaOH (20 mL) was prepared and cooled in an ice bath. The diazonium salt from step 1 was then added slowly with stirring to the phenol solution. The reaction mixture was then left standing in the ice bath for at least 15 minutes until the crystallization is complete (giving a colored solid). The pH of the solution was adjusted with dilute HCl or NaOH solutions (0.1M) in order to induce precipitation. The orange azo dye was then collected and washed with cold water [9].



Scheme 1: Synthesis of the azo compounds.

4-((4-chlorobenzothiazolyl) diazenyl)phenol (AB-4Cl):

Chemical Formula: $C_{13}H_8ClN_3OS$, Orange solid, Yield 65% ; m.p $215^{\circ}C$, ^1H-NMR δ : 6.965 – 7.845 ppm (m, 7H, Ar-H), 10.56 ppm (s, 1H, OH), IR (cm^{-1}), 3488 (OH), 3075 (C-H Ar), 1589 (C=N), MS (m/z) 289 [M^+], Elemental Analysis (Calcd) found: C (53.89) 54.03, H (2.78) 2.83, N (14.50) 14.68.

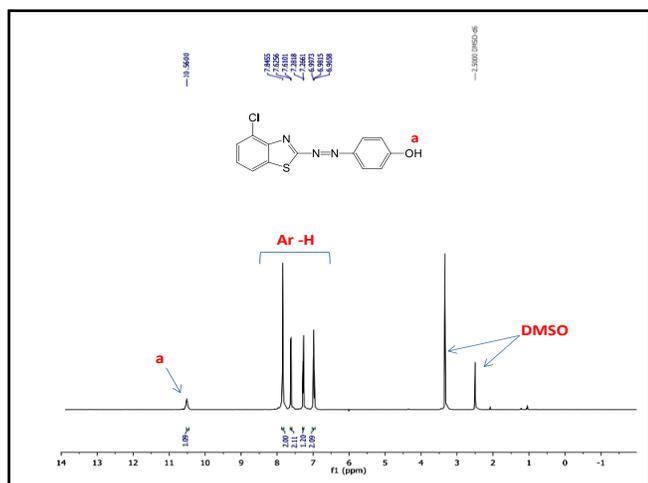
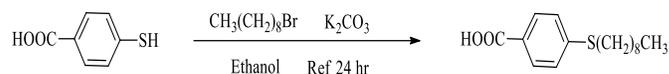


Fig 2: ^1H-NMR spectra for AB – 4Cl

3-chloro-4-((4-chlorobenzothiazolyl) diazenyl) phenol (AB-3,4Cl): Chemical Formula $C_{13}H_7Cl_2N_3OS$, Orange solid, Yield 65% ; m.p $221^{\circ}C$, ^1H-NMR δ : 6.287 – 7.475 ppm (m, 6H, Ar-H), 10.75 ppm (s, 1H, OH), IR (cm^{-1}): 3465 (OH), 3247 (C-H Ar), 1640 (C=N), MS (m/z) 324 [M^+], Elemental Analysis (Calcd) found: C (48.16) 48.23, H (2.18) 2.22, N (12.96) 13.10.

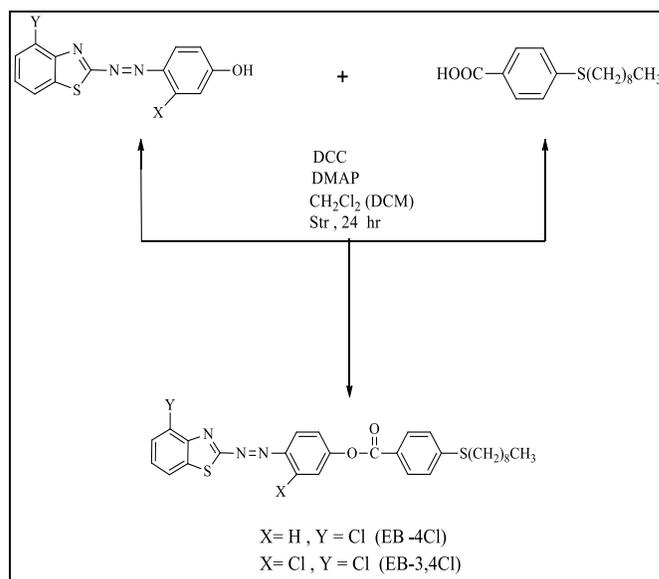
Synthesis of 4- Nonylthio benzoic acid

4- Nonyl thio benzoic acid was synthesized by modification of a literature method [10].



Synthesis of esters

Solutions of 4-(nonylthio)benzoic acid (1 mmol), azo compounds (1mmol) and 1,3-dicyclohexylcarbodiimide (DCC, 1mmol) in dry chloroform (50 mL) containing solid 4-dimethylaminopyridine (DMAP, 1 mmol) as catalyst were magnetically stirred at room temperature for 12 h. The by product (dicyclohexylurea) was filtered off under suction and the solvent was removed on a rot vapor. The crude product was recrystallized from hot ethanol [11].



Scheme 2: Synthesis of the ester compounds.

4-((4-chlorobenzothiazolyl) diazenyl)phenyl 4

(nonylthio)benzoate: (EB-4Cl): Chemical Formula: $C_{29}H_{30}ClN_3O_2S_2$, Orange solid, Yield 62% ; m.p $120^{\circ}C$, ^1H-NMR δ : 0.867 -0.894 ppm (t, 3H, a), 1.251-1.321 ppm (m, 10H, b), 1.425-1.483 ppm (p, 2H, c), 1.673-1.746 ppm (p, 2H, d), 2.974 – 3.004 ppm (t, 2H, e), 7.2415 – 7.843 ppm (m, 11H, Ar-H); IR (cm^{-1}), 1652 (C=O), 2851-2920 (C-H aliphatic), 1592 (C=N); MS (m/z) 552 [M^+], Elemental Analysis (Calcd) found: C (59.38) 59.61, H (4.98) 5.02, N (7.16) 7.29.

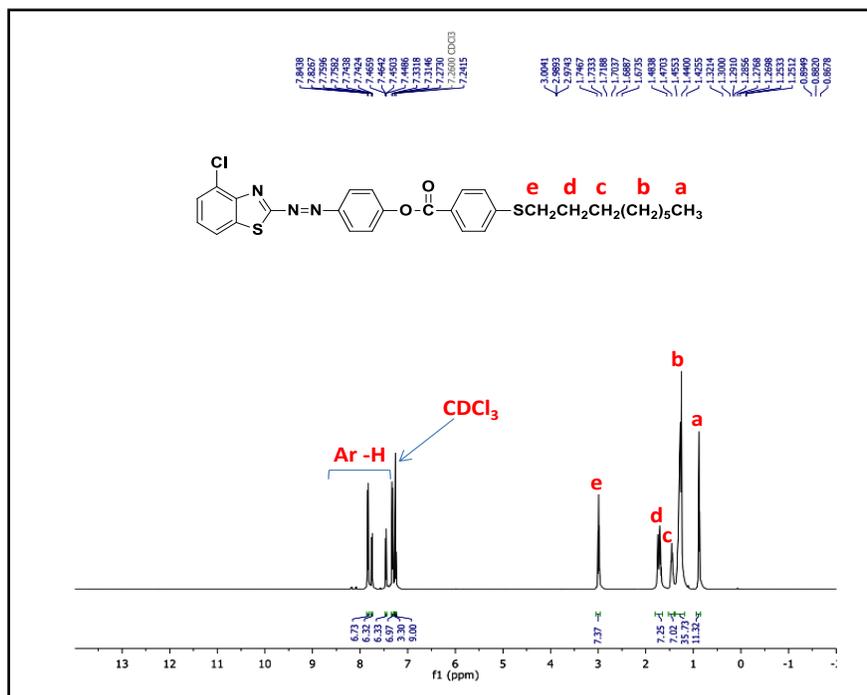


Fig 3: $^1\text{H-NMR}$ spectra for EB – 4Cl

3-chloro-4-((4-chlorobenzothiazolyl)diazenyl)phenyl 4-(nonylthio)benzoate (EB₂-3,4Cl) :Chemical Formula: $\text{C}_{29}\text{H}_{29}\text{Cl}_2\text{N}_3\text{O}_2\text{S}_2$, Orange solid, Yield 62% ; m.p. 115 °C, $^1\text{H-NMR}$ δ : 0.869 -0.896 ppm (t, 3H, a), 1.252-1.315 ppm (m, 10H, b), 1.430-1.490 ppm (p, 2H, c), 1.681-1.742 ppm (p, 2H, d),

2.987 – 3.017 ppm (t, 2H, e), 7.247 – 7.856 ppm (m, 10H, Ar-H); IR (cm^{-1}), 1652 (C=O), 2851-2920 (C-H aliphatic), 1592 (C=N); MS (m/z) 586 [M^+], Elemental Analysis (Calcd) found : C (59.38) 59.69, H (4.98) 5.01, N (7.16) 7.37.

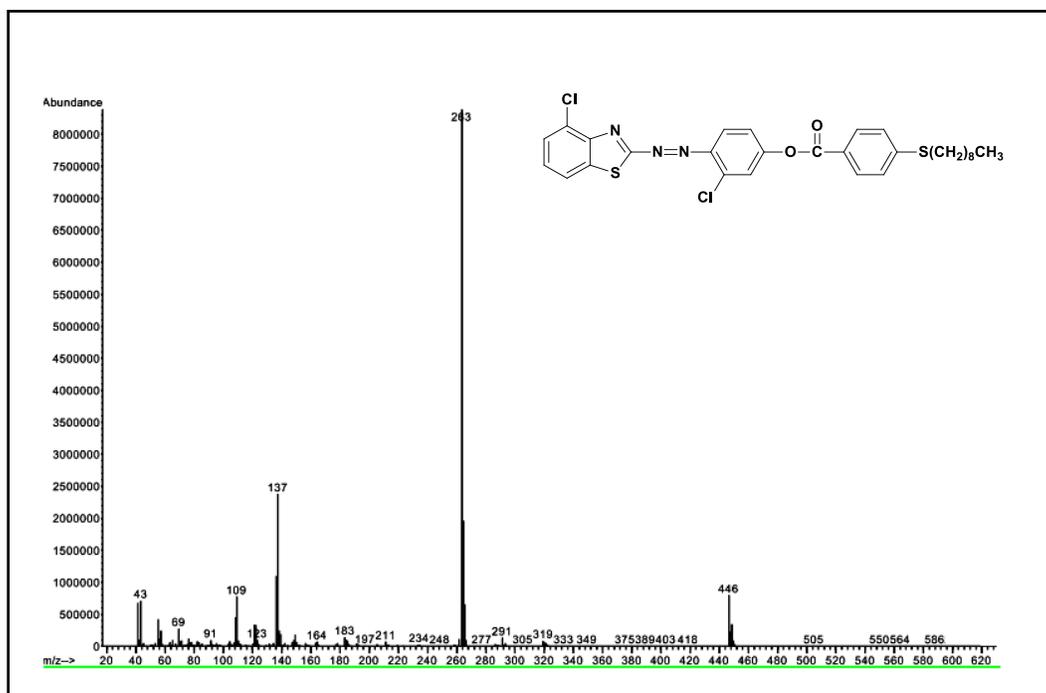


Fig 4: Mass spectra for EB – 3,4Cl

Results and Discussion

The introduction of a substituent into a side position in the molecule of a mesomorphic compound as two opposing effects

on the thermal stability of the mesophase. Firstly, the substituent changes the molecular polarizability and this may increase the thermal stability of the mesophase. However, the size of the side

group broadens the molecule and in doing so decreases the length/breadth ratio and hence the mesophase thermal stability. The second of these effects predominates normally, but the destabilizing effect on the mesophase can be minimized by using a small substituent such as fluorine [12]. The probability that a compound will exhibit a smectic or nematic mesophase depends on the degree of difference between the terminal and lateral attractions. Smectic properties are most often observed when the lateral to terminal ratio is high and the nematic phase appears when the opposite occurs. The replacement of the hydrogen at the 3- positions of azo compounds by lateral introduces an additional dipole moment across the long axis of the molecules which enhances the intermolecular lateral attractions so that the smectic phase should appear for the substituted compounds, but instead the observed mesophase is nematic phase [12, 13].

The thermal mesomorphic properties of the compounds were analyzed by differential scanning calorimeters (DSC) and hot stage polarizing microscopy (POM), which affirm liquid crystal behaviors and their transition temperatures. All the compounds don't have liquid crystalline properties.

Liquid crystalline properties did not appear in the compounds EB – 4Cl and EB – 3,4Cl as a result of presence of chlorine atom at site 4 in benzothiazole ring is outside the molecule plane, causing spatial obstruction and molecular incompatibility, which is increase the molecular width and non – appearance of liquid crystalline properties [12]. The dipole moment, length, width of the molecules plus the length of the bonds were theoretically calculated (table .1, Fig .4, Fig. 5). The results of the theoretical study concurred with the results at the study of liquid crystalline properties using polarized optical microscope.

Table 1: The results of the theoretical study for ester compounds

Compound	Total dipole moment	Length of molecules (°A)	width of the compensated ring with a side group (°A)	Length of the band C-X (°A)	width of thizole ring (°A)
EB – 4Cl	6.5605 Debye	29.088	4.600	1.786	2.671
EB – 3,4Cl	6.4347 Debye	28.881	4.527	1.708 1.711	2.602

(°A): Angstrom

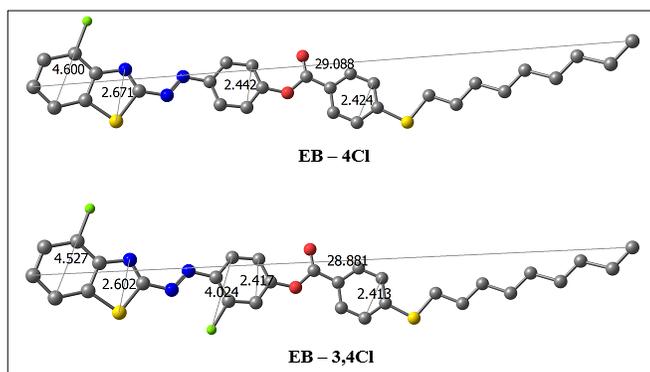


Fig 4: Molecular Length and Width for Compounds

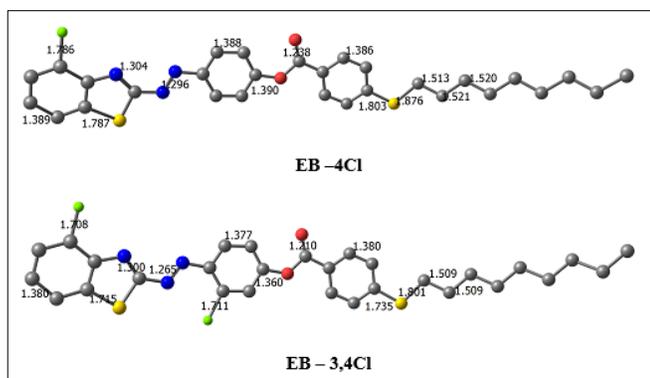


Fig 5: length of bonds for Compounds

Conclusions

New compounds with lateral groups on the central benzene nucleus and benzothiazole ring were synthesized. The study indicated of lateral groups and their position adversely affects on

the mesomorphic properties of these compounds. To support practical results a theoretical study was conducted.

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