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Synthesis, Identification, Physical Properties, Studying of Liquid Crystalline Behavior of New Benzothiazole Derivatives

Nagham Mahmood Aljamali*, Sajida Hadi Ridha, and Noorhan Ali Hamza
Chemistry Department, Factuality of Education for Girls, Kufa University, Iraq.
***Corresponding author: E-Mail: dr.nagham_mj@yahoo.com**

ABSTRACT

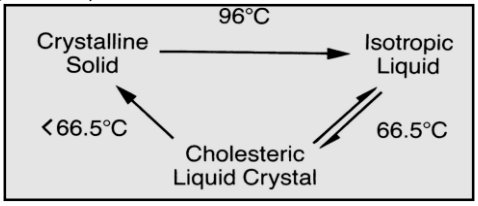
Our work involved synthesis of series benzothiazole derivatives (six compounds) as liquid crystalline compounds which included (Schiff base, ester, amide) in same liquid and have terminal (OR, NH_2, OH, OCH_3) in their structures. Studying of terminal effect in their structures on liquid crystalline behavior. All reactions are followed by TLC chromatography technique and all the formatted compounds have been investigated by using various techniques, like (^{1}H.NMR- proton spectra, ^{13}C.NMR- carbon spectra, (C.H.N)- Micro analysis, FT.IR-infra red spectra), melting points and physical properties. Then studying of liquid crystalline behavior by using polarized optical microscope (POM) with differential scanning calorimeter (DSC) which showed liquid crystal phase in our compounds.

KEY WORDS: Liquid Crystal, DSC, Imine, Polarized Microscope, Hetero Cyclic, Thiazole.

1. INTRODUCTION

Liquid crystals were discovered at the end of the nineteenth century. At the time, there was a protracted and often acrimonious debate concerning the right of discovery and relative claims of priority. However, both Otto Lehmann, a German physicist and Freidrich Reinitzer, an Austrian botanist contributed considerable amounts of knowledge and each deserves recognition (Chandrasekhar, 1992; Demus, 1998).

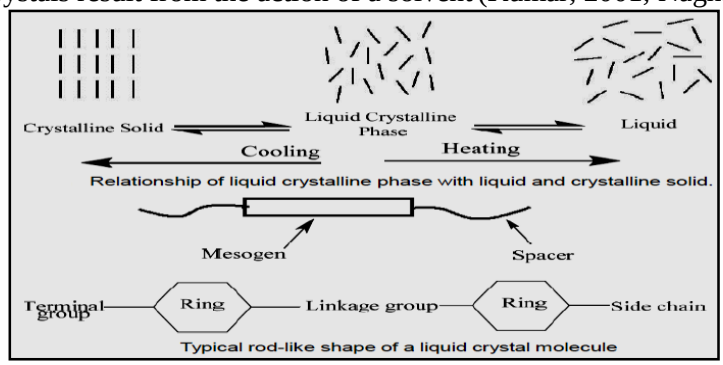
The initial observation and discovery of the liquid crystalline state is usually attributed to Reinitzer in 1888, although scientific literatures written earlier in the nineteenth century describe materials with properties now know to be liquid crystalline (Demus, 2008; Gray, 2009; Demus, 2011). Reinitzer prepared a number of esters of cholesterol in which he observed a new and unusual melting phenomenon of the compounds he studied. Matter conventionally exists in three forms-solid, liquid and gas. Solids may be either crystalline or amorphous. Although liquid crystals exhibit certain aspects of both the solid and liquid phases (Reinitzer, 1888; Lehmann, 1990; Friedel, 1922), the materials also possess their own unique properties that are not found in either solids or liquids individually. For example, their ordering properties can be controlled by electric and magnetic fields; some have optical activity of a magnitude without parallel in any solid, liquid or gas, and some change color as a result of the sensitivity of their structure to temperature. Many different types of liquid crystal exist. A major division arises as a result of the two different ways in which the molecular order of the parent solid can be broken down. These two main classes can then be subdivided into a number of additional distinct types on the bases of their different structures and properties (Brown, 1957; Gennes, 1995; Collings, 1997).



Scheme.1. Phase transitions of cholesterol chloride showing existence of monotropic mesophase

Liquid crystals can be divided into two main classes according to the principal means of breaking down the complete molecular order of the parent solid. This is the major division among liquid crystals; the two types are called Lyotropic and Thermo tropic.

Lyotropic liquid crystals result from the action of a solvent (Kumar, 2001; Nagham, 2016; Oswald, 2005).



Scheme.2. Relationship of Compound structure with its phase

When certain compounds are treated with a solvent. A true solution is not obtained and the resulting state possesses characteristics of the liquid crystalline phase (Nagham, 2017; Bahadur, 1993; Martellucci, 1992). Lyotropic mesophases can be destroyed or converted into isotropic liquids by an excess of solvent or by heating to sufficiently high temperatures. Soaps, various detergents and polypeptides are materials that form lyotropic liquid crystals (Nagham, 2016; Chaikin, 2002; Yang, 2006; Kelker, 1973).

2. INSTRUMENTAL & MATERIALS

- Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected.
- FT-IR spectra were recorded by using (FT-IR 8300 Shimadzu) in the range (400-4000) cm^{-1} as KBr discs
- (C.H.N.S) Micro analysis of elements in Canada.
- 1H.NMR– Spectra in DMSO–solvent were carried out in Canada.
- Differential Scanning Calorimetry (DSC) – Thermal Analysis in Canada.
- Polarized Optical Microscope (POM) in Canada.
- Physical with analytical studies carried out in our university.

Experimental part:

Synthesis of Compound (1): 4-hydroxybenzaldehyde was refluxed with (0.01m) of 6-methoxybenzo[d]thiazol-2-amine for (3hrs) in presence of drops of acetic acid in absolute ethanol as a solvent according to literatures (Nagham, 2017), to yield precipitation which filtered and dried then re-crystallized to give compound.

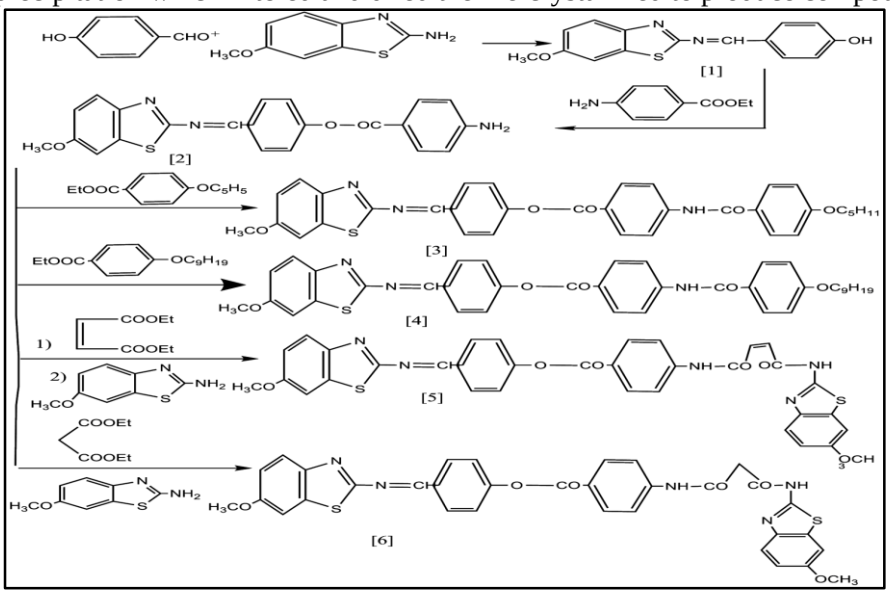
Synthesis of Compound (2): A mixture of compound (0.01mole) was refluxed with ethyl 4-aminobenzoate for (4 hrs) according to literatures (Nagham, 2016), it gave precipitation, filtered and dried then re-crystallized to yield compound.

Synthesis of Compound (3): A mixture of (0.01mole) compound with (0.01mole) of ethyl 4-(pentoxy) benzoate was reacted in refluxing for (5 hrs) in absolute ethanol according to literatures (Nagham, 2017), after that it gave precipitation, filtered and dried then re-crystallized to yield compound.

Synthesis of Compound (4): Compound (0.01mole) was refluxed with (0.01mole) of ethyl 4-(nonyloxy) benzoate compound for (4hrs) in presence of absolute ethanol as a solvent according to literatures (Nagham, 2017), to yield precipitation which filtered and dried then re-crystallized to yield compound.

Synthesis of Compound (5): (0.01mole) of compound was refluxed with (0.01 mole) of (diethyl malate) and (6-methoxy-2-amino-benzothiazole) respectively in presence of ethanol as a solvent, according to studies (Nagham, 2017), then it gave precipitation which filtered and dried then re-crystallized to produce compound.

Synthesis of Compound (6): (0.01mole) of compound was refluxed with (0.01 mole) of (diethyl malonate, 6-methoxy-2-amino- benzothiazole) respectively in presence of ethanol as a solvent, according to studies (Nagham, 2017), then it gave precipitation which filtered and dried then re-crystallized to produce compound.



Scheme.3. Synthesis of Liquid Crystals [1 – 6]

3. RESULTS AND DISCUSION

The present paper involved, preparation of new compounds [1- 6] as a liquid crystals, which identified by using spectral techniques represented by (FT.IR, H.NMR, C.H.N.S- Analysis) and studying some of physical and thermo analysis with chemical applications such as (liquid crystal, thermo – Analysis, Optical microscope).

Organic Investigation:

The FT.IR- Investigation: Absorption bands appeared at (1630-1656)cm^{-1} in all compounds [1 -6] of (C=N) endocycle groups ,and other bands are appeared at {(1660-1699)cm^{-1} for (NH-CO) amide of groups in compounds [3-6] , and amine group (Nagham, 2017) as (CO-NH) at band (3236)cm^{-1} in compound (6), and other bands listed in table.1, and figures.1-6.

Table.1. FT.IR- data (cm^{-1}) of Compounds (1-6)

Comp.	υ (C=N) endocycle	(CH=N) Imine	υ (-COO) ester	(NH-CO) Amide	Other Groups
1	1630	1604	-------	------	(CH)arom:3050, (OH)Phenol:3427, (C-S)endocycle: 713, (C-O-CH_3)Ether:1116, (CH_3)Aliphatic:2900
2	1633	1622	1713	-------	(NH_2)Amine:3292, 3184, (C-S)endocycle:766, (CH)arom:3029, (C-O-CH_3)Ether:1186, (CH_3)Aliphatic:2950
3	1656	1610	1710	1699	(CH)aliphatic:2912, (CO-NH)Amine:3240, (C-S)endocycle:734, (CH)arom:3031, (C-O-CH)Ether:1172, 1190
4	1645	1620	1700	1690	(CO-NH)Amine:3266, (C-S)endocycle:700, (CH)arom:3032, (C-O-CH_3)Ether:1186, (CH)Aliphatic:2900
5	1640	1620	1700	1678, 1660	(CO-NH)Amine:3286, (C-S)endocycle:755, (CH)arom:3080, (C-O-CH)Ether:1174, (CH)Aliphatic:2978, (CH=CH)Alkene:3100
6	1647	1613	1730	1683, 1695	(CO-NH)Amine:3236, (C-S)endocycle:761, (CH)arom:3022, (C-O-CH)Ether:1176, (CH)Aliphatic:2950

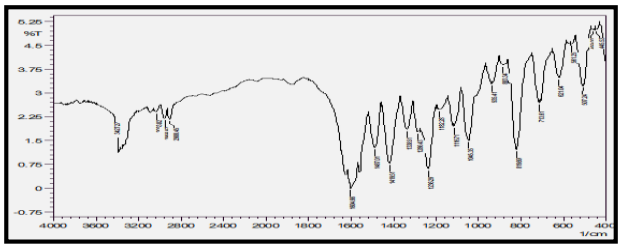


Fig.1. FT.IR of Compound [1]

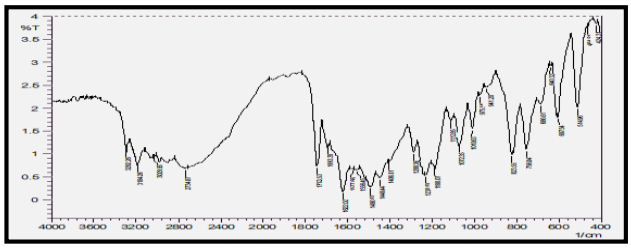


Fig.2. FT.IR of Compound [2]

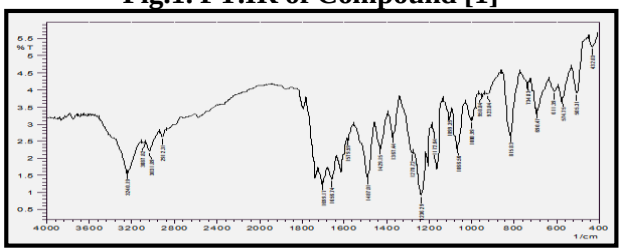


Fig.3. FT.IR of Compound [3]

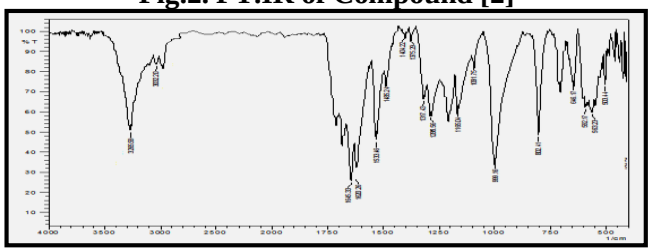


Fig.4. FT.IR of Compound [4]

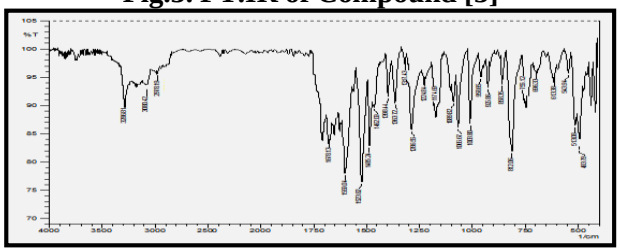


Fig.5. FT.IR of Compound [5]

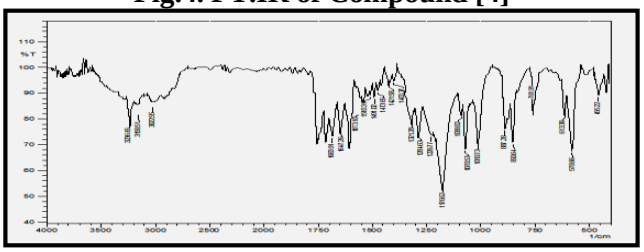


Fig.6. FT.IR of Compound [6]

The ^{1}H.NMR- Spectra: showed signals at ɓ {ɓ(6.79-7.83) for protons of phenyl ring and heterocycle in compounds [1, 6] respectively. While compounds [3, 6] showed signal at ɓ (9.68-9.69) for proton of (NH-CO) amide, compound [2] appeared peak at ɓ (5.60) for NH_2 group}, and other signals in table.2, and figures.7-12.

Table.2. H.NMR-data (δ - ppm) of Compounds [1-6]

Comp.	Phenyl ring, Heterocycle	CH=N Imine	NH, NH_2 Amine	NH-CO Amide	Other groups
1	6.79-7.87	8.20	---	---	DMSO-d6(solvent):2.50, (OH)Phenol:10.95, (OCH_3)Ether:3.41
2	6.58-7.93	8.62	5.60	---	(OCH_3)Ether:3.85, DMSO-d6(solvent):2.50
3	7.16-7.89	8.33	---	9.68	(O-CH_2-):(3.45-3.65), (O-CH_3):(3.93), (-CH_2)$_4$ Chain:(0.75- 2.25)
4	6.96-7.93	8.62	---	9.00	(O-CH_2-):(3.85-3.04), (O-CH_3):(4.10), (-CH_2)$_8$ Chain:(0.74-2.26), DMSO-d6(solvent):2.50
5	6.56-7.98	8.26	---	9.00, 9.30	(O-CH_3):(3.41), (CH=CH)Alkene:(5.60, 5.73)
6	7.27-7.83	8.31	---	9.69	(O-CH_3):(3.34), (CO-CH_2-CO):2.01

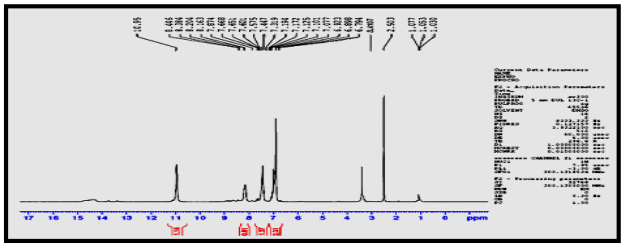


Fig.7. H.NMR of Compound [1]

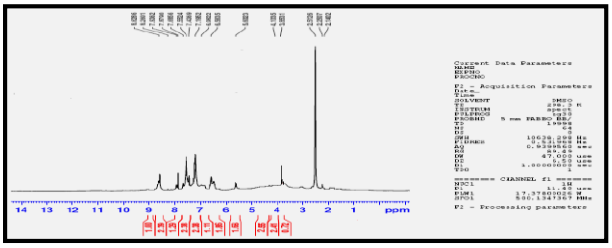


Fig.8. H.NMR of Compound [2]

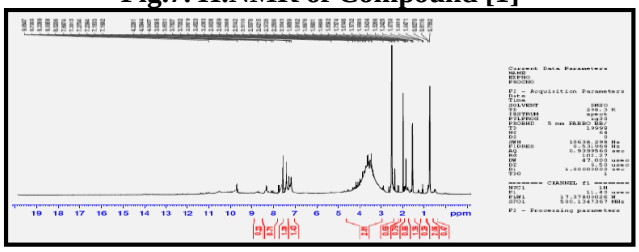


Fig.9. H.NMR of Compound [3]

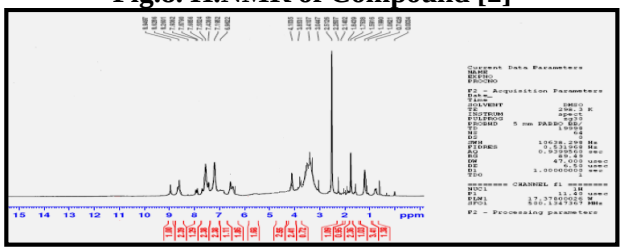


Fig.10. H.NMR of Compound [4]

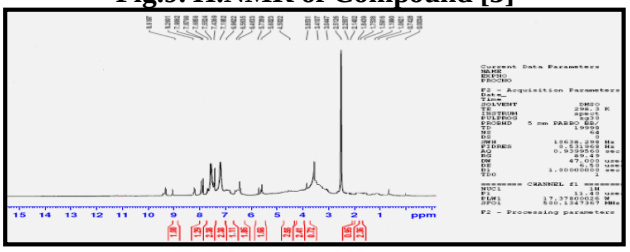


Fig.11. H.NMR of Compound [5]

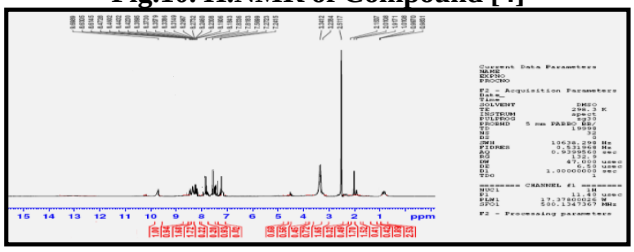


Fig.12. H.NMR of Compound [6]

Studying of Polarized Optical Microscope: This work involved studying of phases of compounds, behavior of compounds as a liquid crystals by following with optical microscope through heating compounds with different temperatures.

From results, we found compounds (3-6) are liquid crystals, figures (13-16) for the compounds by optical microscope measurements are shown.

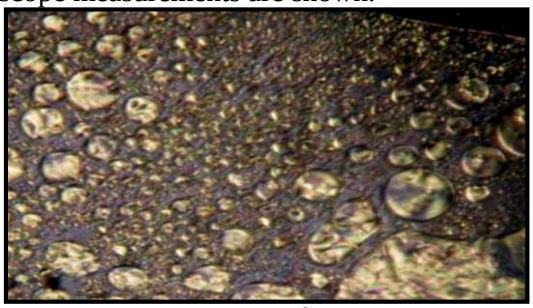


Fig.13. Crystal Phase at (40^{0}C) for Compound [3]

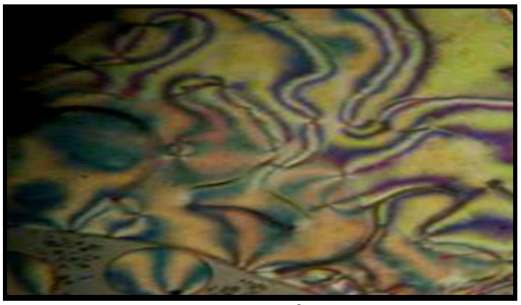


Fig.14. Crystal Phase at (35^{0}C) for Compound [4]

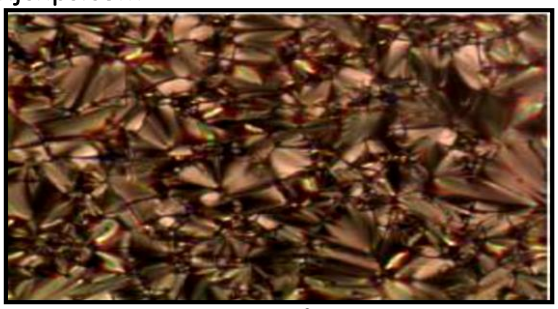


Fig.15. Crystal Phase at (30^{0}C) for Compound [5]

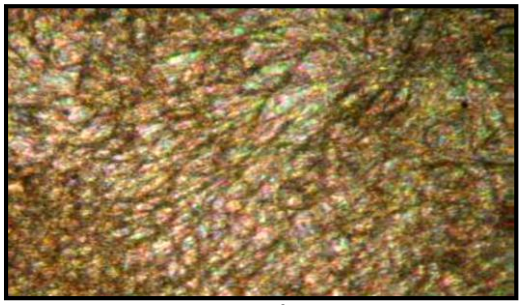


Fig.16. Crystal Phase at (30^{0}C) for Compound [6]

Thermal Studying (DSC – Measurements): DSC – measurements of compounds measured for stability of (hetero cycles- azomethine and amide or ester) compounds or ether compounds in some figures (17-20), DSC- Curves showed high stability toward high temperature.

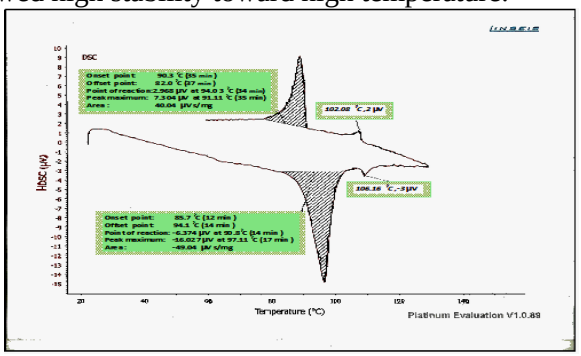


Fig.17. DSC of Compound [3]

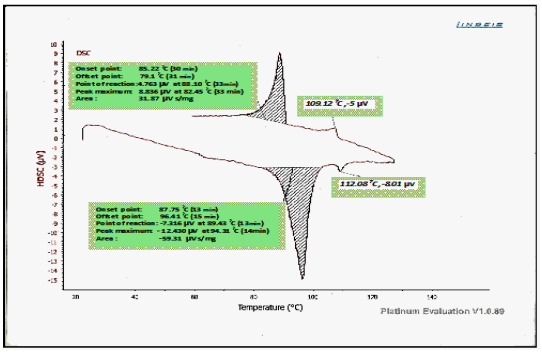


Fig.18. DSC of Compound [4]

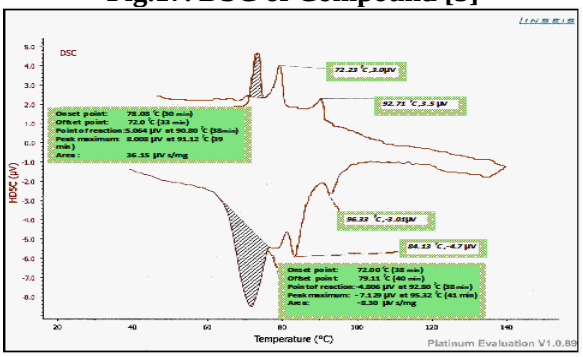


Fig19. DSC of Compound [5]

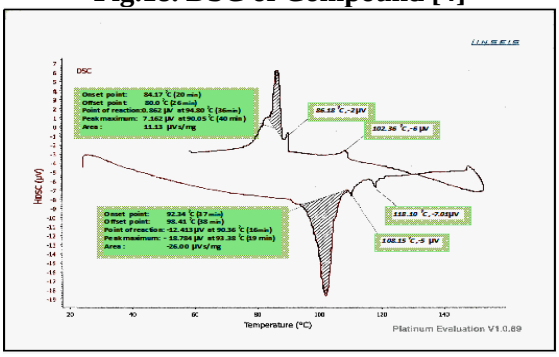


Fig.20. DSC of Compound [6]

Table.4. Calculations of Thermodynamic Data of Liquid Crystals (Heating)

Comp.	M.W.	ΔH, j/g			ΔT/k			ΔH, KJ/mol			Δs		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
3	593.69	49.04	3	---	362.9	379.1	---	29.1	1.7	---	0.08	0.004	---
4	649.80	59.3	8.01	---	365.08	385	---	38.5	5.2	---	0.1	0.013	---
5	667.75	8.30	4.7	3.01	348.5	357.13	369	5.5	3.1	2.003	0.01	0.008	0.005
6	651.71	26	5	7	368.3	381.15	391	16.9	3.2	4.5	0.04	0.008	0.011

Table.5. Calculations of Thermodynamic Data of Liquid Crystals (Cooling)

Comp.	M.W.	ΔH, j/g			ΔT/k			ΔH, KJ/mol			Δs		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
3	593.69	-2	-40.4	---	375.5	359.15	---	-1.18	-23.9	---	-0.003	-0.066	---
4	649.80	-5	-31	---	382.2	355.16	---	-3.24	-20.14	---	-0.008	-0.056	---
5	667.75	-3.5	-3	-36.15	365.71	345.23	348.01	-2.33	-2.003	-24.1	-0.006	-0.005	-0.069
6	651.71	-6	-2	-11	375.36	359.15	375.63	-3.91	-1.303	-7.16	-0.010	-0.003	-0.019

(C.H.N.S)- Micro Analysis: From Results of micro analysis of liqud crystals, it was found the calcated data cmopactable with experimental data, all data are listed in table.6.

Table.6. Micro Aalysis of Compounds

Compound	M.F.	Calc./Found (%)			
		C	H	N	S
1	$C_{15}H_{12}N_2O_2S$	67.164/66.801	4.477/4.189	10.447/10.101	11.940/11.482
2	$C_{22}H_{17}N_3O_3S$	65.508/65.074	4.218/4.027	10.421/10.137	7.940/7.591
3	$C_{34}H_{31}N_3O_5S$	68.802/68.217	5.227/4.913	7.082/6.863	5.396/5.109
4	$C_{38}H_{39}N_3O_5S$	70.261/69.873	6.009/5.755	6.471/6.153	4.930/4.609
5	$C_{34}H_{25}N_5O_6S_2$	64.864/64.285	3.974/3.452	13.354/13.197	5.087/4.782
6	$C_{33}H_{25}N_5S_2O_6$	60.829/60.222	3.840/3.462	10.752/10.352	9.831/9.397

Physical and Chemical Properties: Physical and chemical properties represented by (R_f) of TLC- Technique for following the reactions, type of solvent which are used in TLC – Plate, and products from reactions %, all data are listed in table.7.

Table.7. Some Physical and Chemical Properties for Compounds [1–6]

Compound	M.F.	Color	Product %	Rf	TLC solvents Ethanol:Benzene
1	$C_{15}H_{12}N_2O_2S$	Yellow	72	0.70	1:4
2	$C_{22}H_{17}N_3O_3S$	Yellowish brown	70	0.68	1:4
3	$C_{34}H_{31}N_3O_5S$	Deep Yellow	70	0.70	1.5:3.5
4	$C_{38}H_{39}N_3O_5S$	Yellow	74	0.72	1.5:3.5
5	$C_{34}H_{25}N_5O_6S_2$	Yellowish Orange	72	0.66	1.5:3.5
6	$C_{33}H_{25}N_5S_2O_6$	Pale Orange	70	0.64	1.5:3.5

4. CONCLUSION

The synthesized liquid crystals involved (amide, ester, ether) in there structures which gave it more stability properties, various chemical with physical properties due to types of functional groups.

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