Synthesis ,characterization and mesomorphic properties of some azo – Schiff base liquid crystalline compounds

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Abstract :

Five azo Schiff base liquid crystalline compounds with different polar groups named (D_1S, D_2S, D_3S, D_4S, D_5S)have been synthesized and their structures were characterized using FTIR spectrometry technique , while their liquid crystalline phase transition and temperature range was confirmed by differential scanning calometery which indicate the presence of liquid crystalline phases with a relatively different temperature ranges. The textures of the synthesized liquid crystalline compounds were performed using polarized optical microscope which show a clear nematic phases with a thread and droplets like nature with a wide temperature range between (23.52 - 43.23 ^{o} C) with the exception of the two compounds (D_2S, D_3S) which shows a smectic phase of few temperatures ranging between (12.5 - 14.71 ^{o} C) in addition to the nematic phase stated above .

For the purpose of geometry optimization of structures of chemical compounds prepared in this research we have been use of the computer program known (Alchemy 2000 version 1), in which the optimization for the studied structures of liquid crystalline compounds confirmed the required linearity for mesophase formation , we then obtained values of the electric dipole of these compounds, which has been found to be in the range (0.7565 - 3.7547 Deby) .

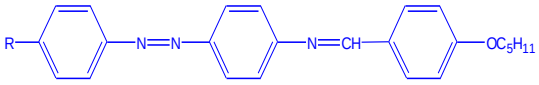
Key word : azo ,Schiff base , photoisomerization , geometry optumization , dipole moments.

1- Introduction :

Azo compounds have been of almost importance in many miscellaneous application areas such as reversible optical storage, nonlinear optical (NLO) devices and liquid crystalline displays (LCDs)[Bauman D. *et al.* , 2009 , Advincula RC. *et al.*2001 , Delaire J. *et al.* 2000] .

Another reason behind the ever-expanding interest in preparation of azo compounds containing Schiff-base ligands lies in their wide use as dyestuff in textile industry which is prominently due to their excellent coloring features. As well as all aforementioned applications, they also can be utilized in photonic devices, electro-optic modulators and components of optical communication systems owing to their second order nonlinear optical properties. Hence, it is no wonder why these kinds of dyes have been the matter of discussion in recent research [Klysubun P. *et al* .2002 , Fuh A. *et al.* 2000].

Our efforts in this research has been directed toward synthesis of some azo Schiff base liquid crystalline compounds with different polar groups regarding that such compounds with azo groups may show substantial photo chromic effects, it can be deduced that such linear systems having azo benzene and azomethine moieties (Schiff-bases) would be exceptionally promising for wide variety of new technological applications[Blanche A. *et al.*1997, Yadav S. *et al.*2011] .Scheme (1) show the structure of the studied compounds .



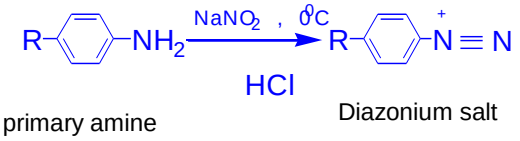
R= SO_3H , Br , COOH , $COCH_3$, CH_3CH_2Co

Scheme (1) The general structure of the synthesized azo Schiff base compounds

2- Expermental :

2.1 Synthesis of azo Schiff base liquid crystalline compounds In the first step we have been synthesis a diazonium salts from five different primary amines using atypical procedure from the literature [Senadeera G. *et al.*2005 , Park, J. *et al.*2009] . by dissolving (0.002 mole) of Na_2CO_3 in (12 ml) of distilled water ,and then addition of (0.0057 mole) from the primary amine such as salfanalic acid and heating until it dissolve completely , then after filtration and cooling using ice bath (0- 5 $^{\circ}C$) we add (0.0054 mole) of ($NaNO_2$) and stirring ,then by adding (1.25 ml) of

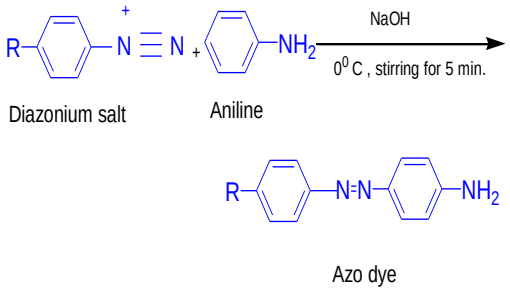
HCL drop by drop we observe the emission of chlorine gas and this guide to get the diazonium salt of such primary amine in excellent yields , Scheme (2) show the general synthesis root for diazonium salts .



R= SO_3H , Br , COOH , $COCH_3$,CH_3CH_2CO

Scheme(2) synthesis root for the diazonium salts

The azo dye (amino azo benzene) was then synthesized in the second step via coupling reaction with aniline using a well known procedure [Norman R.*et al.* 2009 , Florian H.*et al.*2009]. a mixture of aniline (0.0057 mole) and glacial acetic acid (0.5 ml) was added to the diazonium salt prepared in the first step as a drops with continue stirring and cooling for 15 min ,then we get a precipitate which differ in colure for different primary amines ,then by adding (7.5 ml)from 10% NaOH and checking by using pH paper until the solution become abasic , then we add NaCl and filtering the produced solution which kept for 24 houre's , the precipitate was then collected which represents the target amino azo benzene as given in Scheme (3).



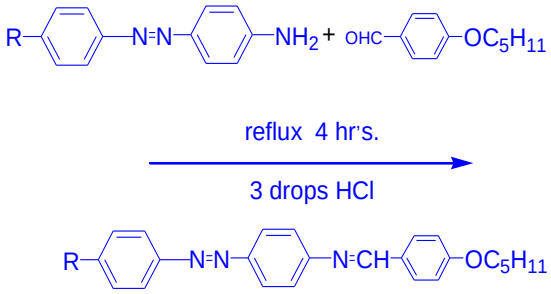
R= SO_3H , Br , COOH , $COCH_3$, CH_3CH_2Co

Scheme (3) synthesis root for azo dye (amino azo benzene)

The third step consist of the condensation reaction for amino azo benzene that is synthesized in the second step with the previously synthesized 4-pentyloxy benzaldehyde [Hassan H.*et al.*2013].

In (250 ml) round bottom we put (0.01 mole) of 4- pentyloxy benzaldehyde dissolved in (10 ml) from absolute ethanol ,then by adding 0.01

mole from the amino azo benzene dye dissolved in 10 ml absolute ethanol with three drops of HCl and reflux the mixture with stirring for 3hr's. , ayelow precipitate was collected , then after filtration and drying the product was recrystalized two times from ethanol to get the azo Schiff base compounds as shown in Scheme (4) .



R= SO_3H , Br , COOH , $COCH_3$, H_3CO

Scheme (4) synthesis root for azo Schiff base compounds

2-2-Characterization :

2-2-1- IR spectroscopy :

All the synthesized azo dyes and azo Schiff base compounds were characterized by using SHIMADZU - IR spectrophotometer model (IRAffinity-1S Fourier Transform Infrared Spectrophotometer) and the stretching vibrations of functional groups in the synthesized compounds was found in a good agreement with other researchers [Weissflog W. *et al.* 2001 , Emandi A. *et al.*. 2010 , Prajafati K. *et al.* 2004]. The IR spectrum for one azo dye sample (D_1)and one azo Schiff base compound (D_1S) was given in figure(1) and figure (2) respectively.

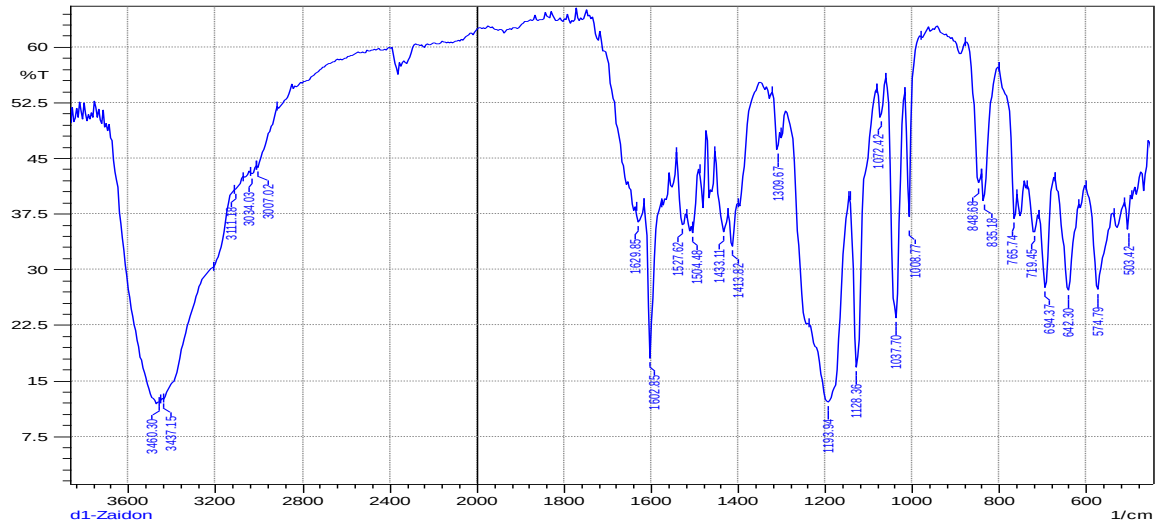


Fig.(1):IR spectrum for azo dye sample D_1

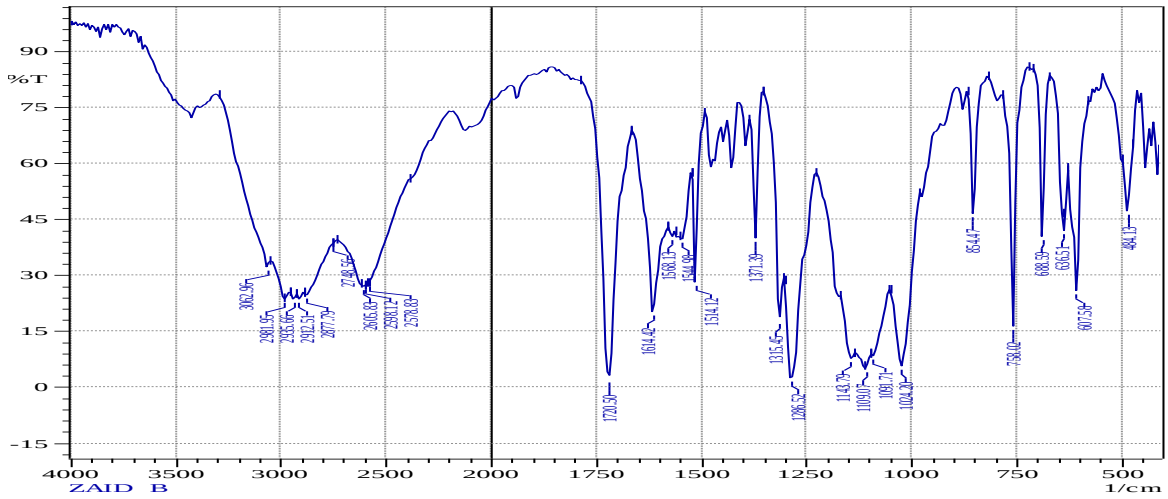


Fig.(2) : IR spectrum for azo Schiff base sample D_1S

The vibration frequency of the important functional groups in the synthesized azo dye and azo Schiff base compounds was given in table (1) and table (2) respectively.

Table (1) : important functional groups in azo dye samples

Compound	**N=H st.**	**C=H st. aromatic**	**N=N st. azo**	**C=O st.**	**C=C st. aromatic**	**Other specific bands**
D_1	3460 - 3437	3034	1602	------	1527	S=O st. at 765
D_2	3446 - 3401	3021	1604	1689	1529	C-H aliphatic at 2850 - 2949
D_3	3445 - 3408	3026	1600	-----	1571	C-Br st. At 650
D_4	3440- 3331	3062	1600	1656	1587	-----
D_5	3401 - 3333	3024	1604	1678	1541	-----

Table (2) : important functional groups in azo schiff base samples

Compound	**C=H st. aromatic**	**C=H st. aliphatic**	**N=N st. azo**	**CH=N st.**	**C=C st. aromatic**	**Other specific bands**
D_1S	3304	2860 - 2940	1556	1697	1590	S=O st. at 761
D_2S	3090	2872 - 2939	1602	1689	1575	C=O st. Ester at 1716
D_3S	3055	2883 - 2930	1606	1672	1577	C-Br st. at 650
D_4S	3095	2872 - 2989	1602	1681	1575	C=O st .ketone at 1716
D_5S	3060	2872 - 2941	1600	1678	1575	C=O st. carboxyl at 1687

2-2-2- Differential scanning calorimetery :

The phase transition temperature of the synthesized liquid crystalline compounds in this research were confirmed using DSC technique which indicate a clear transition from solid to nematic liquid crystal and then to isotropic liquid in some studied compounds named D_1S , D_4S and D_5S while the other two samples named D_2S and D_3S show a transition from solid to smectic phase ,then nematic phase as given in fig(3),Fig(4), Fig (5), Fig.(6)and Fig.(7)respectively.

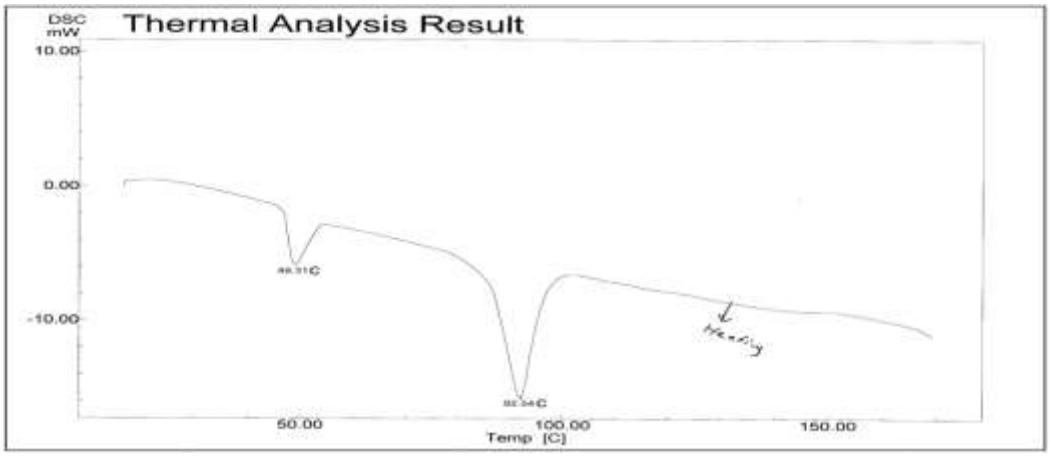


Fig.(3): DSC thermo gram for liquid crystalline compound D_1S

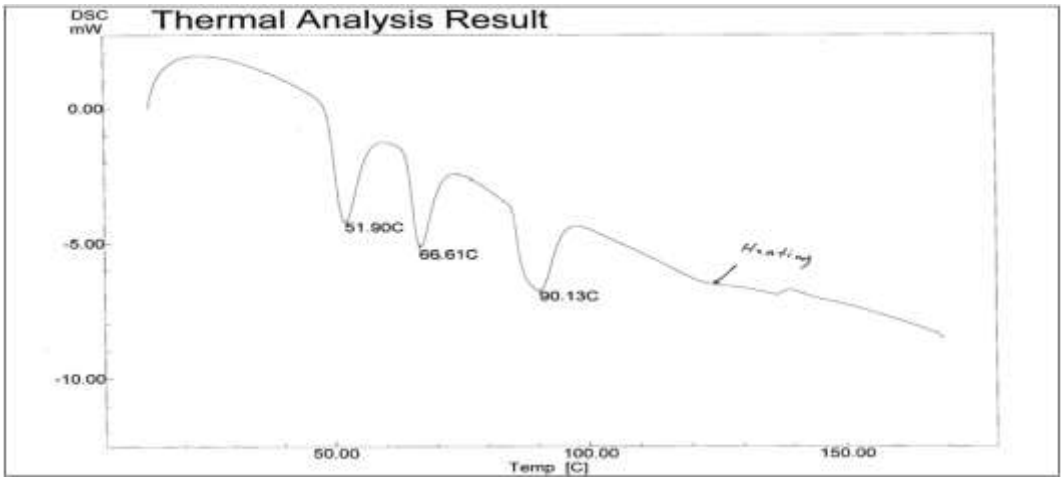


Fig.(4): DSC thermo gram for liquid crystalline compound D_2S

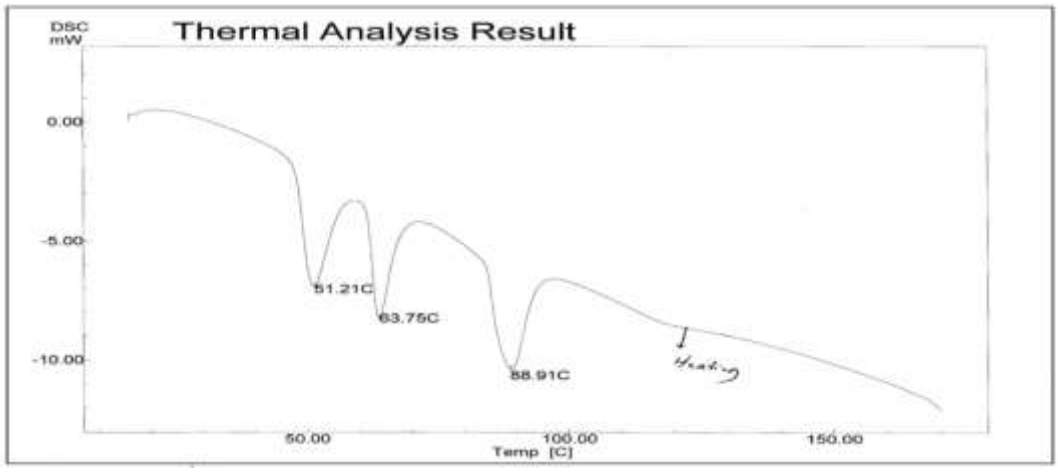


Fig.(5): DSC thermo gram for liquid crystalline compound D_3S

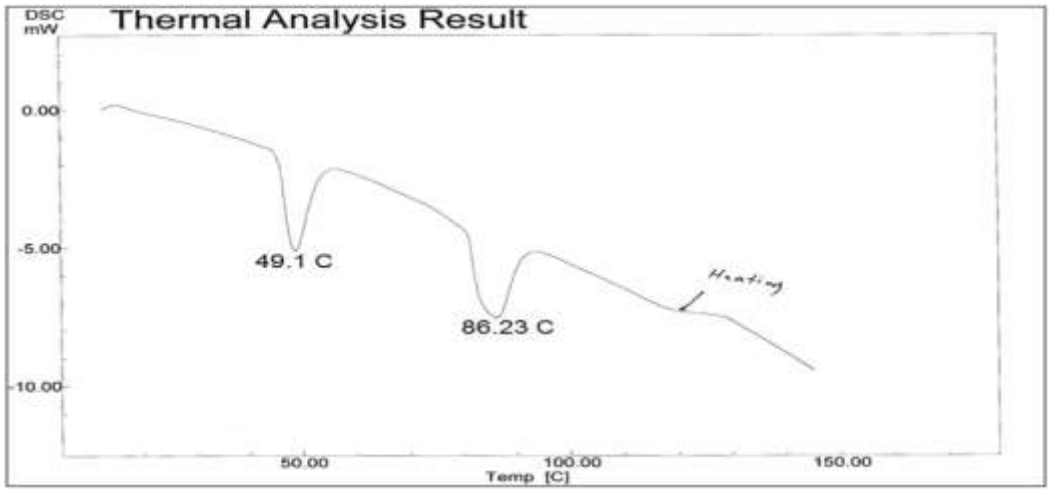


Fig.(6): DSC thermo gram for liquid crystalline compound D_4S

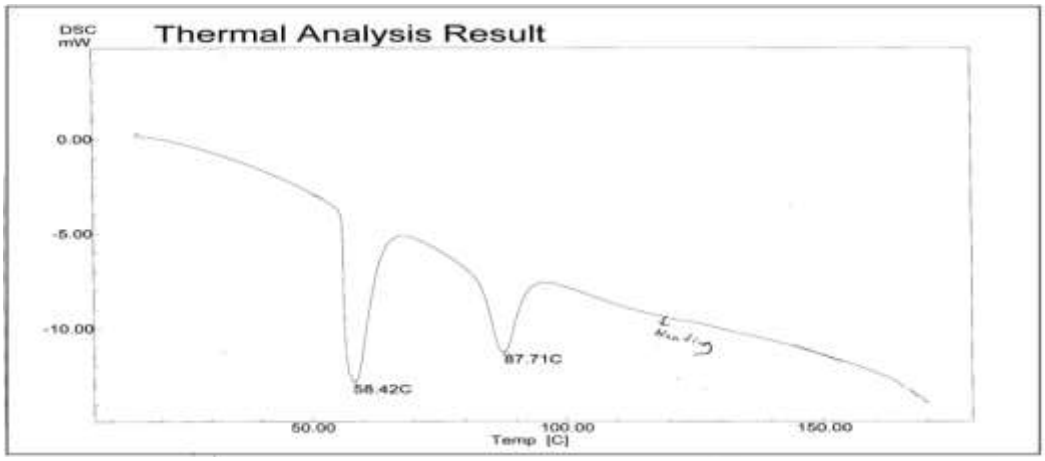


Fig.(7): DSC thermo gram for liquid crystalline compound D_5S

The differential scanning calometry technique used for thermal analysis of the synthesized compounds give a clear evidence that azo- schiff base compounds show a clear liquid crystalline phase transitions with different nematic range .The phase transition temperature as well as the range of transition for the synthesized liquid crystalline compounds was given in table (3).

Table (3) : phase transition and liquid crystalline temperature range for synthesized azo Schiff base compounds.

Sample	Temperature (°C)			Nematic temperature range
	Smectic	Nematic	Isotropic	ΔT□°C
D_1S	-	49.31	92.54	43.23
D_2S	51.9	66.61	90.13	23.52
D_3S	51.2	63.7	88.91	25.21
D_4S	-	49.1	86.23	37.13
D_5S	-	58.42	87.71	29.29

2-2-3- polarized optical microscope:

The textures of the sandwiched glass cell (2X2 Cm^2) of different liquid crystalline samples in this research were investigated through polarized optical microscope model (Steindorff® NYMC59000 Trinocular Polarizing Digital / Video Microscope) equipped with Motic Digital Camera model (Moticam 480)and a hot stage fabricated in the laboratory in which the temperature was measured by a digital thermometer with a thermocouple just in contact with the glass of the cell, figures (8), (9),(10),(11), (12) and (13) show the textures of the prepared liquid crystalline samples respectively.

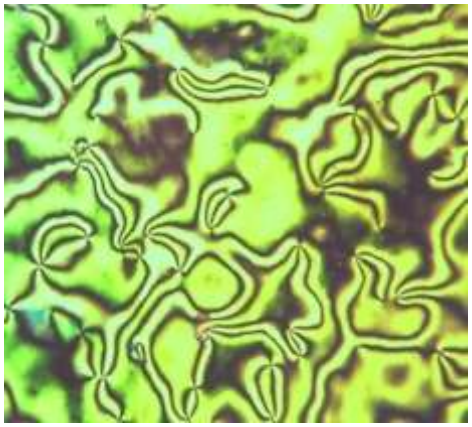


Fig.(8) : nematic thred ike texture for the sample D_1S

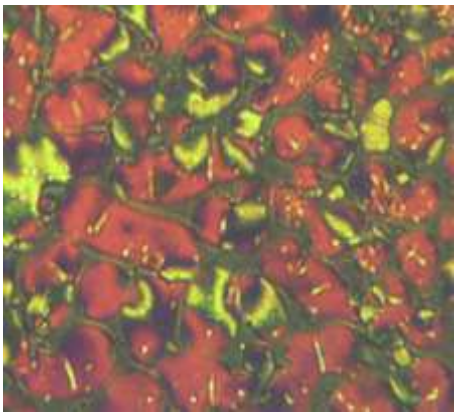


Fig.(9) : nematic drop like texture for the sample D_2S

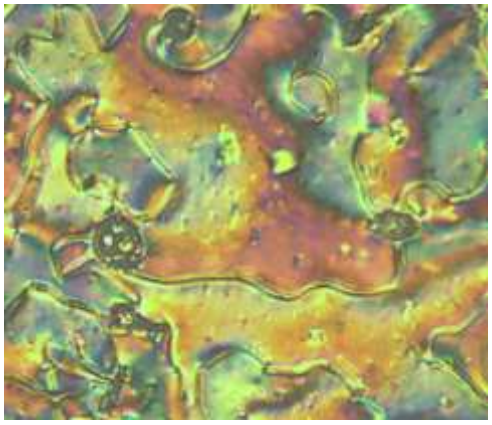


Fig. (10) : smectic phase for the sample D_2S

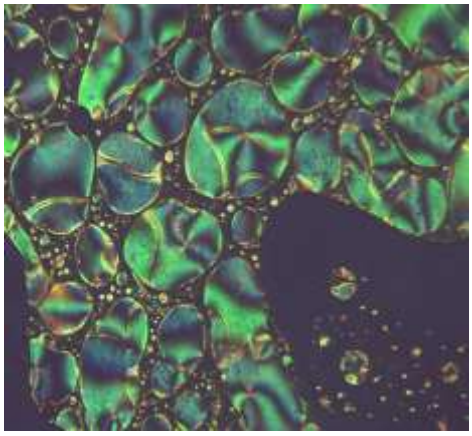


Fig.(11):Nematic drop like textures for the sample D_3

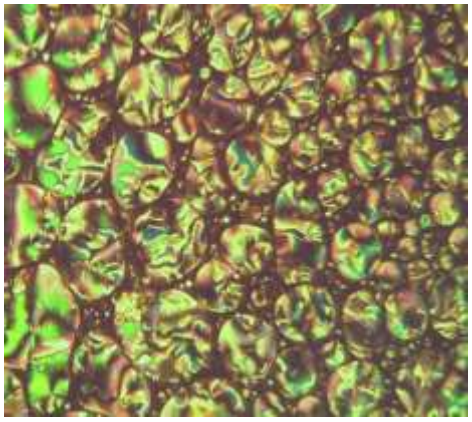


Fig.(12): Nematic drop like texture for the sample D_4S

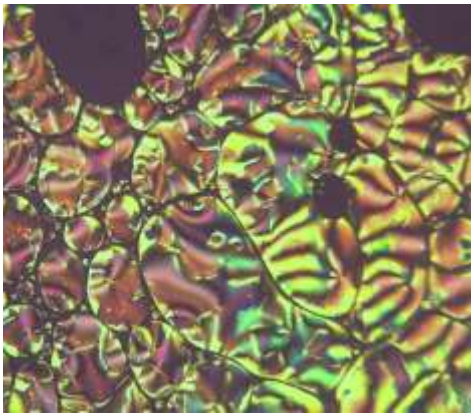
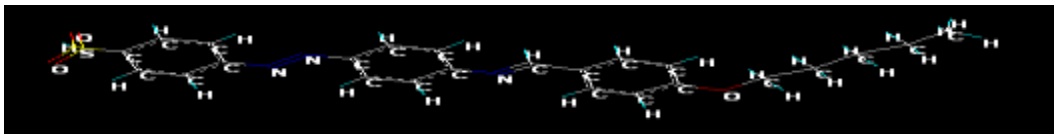


Fig.(13) : Nematic drops of thred like textures for the sample D_5S

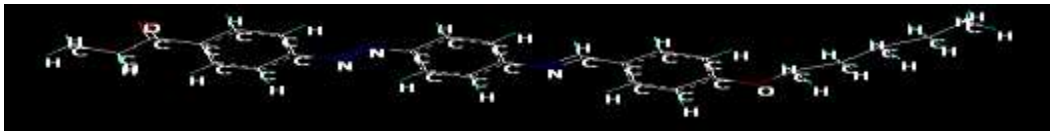
3-Geometry optimization study :

Synthesis of different organics especially liquid crystalline compounds have got a lot of attention recently due to their wide technological applications, therefore many of the software has been developed to keep pace with this development , and one of these is a software program Alchemy 2000 , (version 1) from Tripos, Inc. St.Lous,MO(USA).

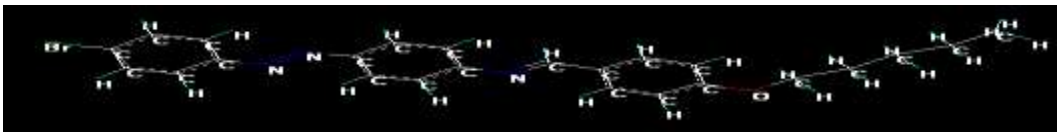
In this research we have been study the geometry optimization of the synthesized liquid crystalline compounds and get their optimized structures as well as some of their molecular properties as given in figure (13) and table (4) respectively.



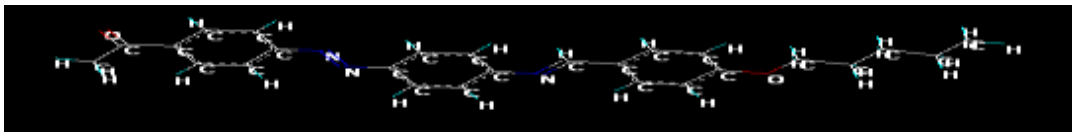
D_1S



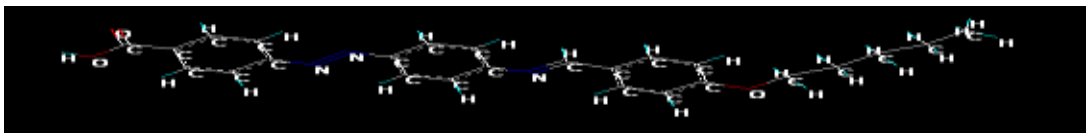
D_2S



D_3S



D_4S



D_5S

Figure (13) : Geometry optimization for different synthesized liquid crystalline structures

Table (4):dipole moments for optimized liquid crystalline compound structures

Sample	Dipole moment (Deby)
D_1S	3.7547
D_2S	0.7565
D_3S	2.8270
D_4S	0.9247
D_5S	2.1414

4- Conclusions :

It is reasonable to say that the synthesized three member ring azo – schiff base compounds with an azo group show a clear liquid crystalline phases and some of them show a polymorphism behavior with an excellent color due to the presence of an azo group that is responsible for the absorption of light .In spite of trans – cis photoizomerization phenomena that may occur for amino azo benzene dyes , the synthesized azo Schiff base compounds mostly show the more stable trans confirmation feature and this will make them exhibit the required linearity for mesophase formation .The different liquid crystalline phases and their temperature range was strongly effected by the different polar groups that is present which consequently enhance dipole-dipole interaction or dispersion forces that is responsible for mesophase formation. Geometry optimization study for the synthesized azo Schiff base compounds confirmed the exhibited linearity for such

samples with different magnitude of dipole moments as expected

from different polar groups in such samples.

5- References :

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تحضير وتشخيص ودراسة الخواص البلوريه السائله لبعض المركبات من نوع ازو- شيف

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الخلاصه

تضمنت الدراسة التحضير وبنجاح لخمسه من المركبات البلوريه السائله نوع ازو- شيف (D_1S , D_2S, D_3S, D_4S, D_5S) ذات المجاميع القطبيه المختلفه، وبعد التاكد من صحة التراكيب الكيميائيه للمركبات المحضره عن طريق مطيافية الاشعه تحت الحمراء (FTIR) تم ايضا التاكد من ان المركبات المحضره تظهر الصفات البلوريه السائله وذلك باستخدام تقنية المسح المسعري التفاضلي (DSC)والمجهر ذو الضوء المستقطب (POM) ، حيث اوضحت الدراسه ان المركبات التي تم تحضيرها نوع ازو شيف اظهرت اطوارا بلوريه سائله من النوع النيماتي واضحه وذات مديات واسعه من درجات الحرارة تتراوح بين (23.52 - 43.23 م$^{\circ}$) للمركبات المختلفه باستثناء المركبين (D_2S , D_3S) واللذين اظهرا الطور السمكتي لمدى قليل من درجات الحراره يتراوح بين (12.5 - 14.71 م$^{\circ}$) بالاضافه الى الطور النيماتي المشار اليه انفا .

ولغرض الحصول على البنيه الهندسيه الامثل للتراكيب الكيميائيه للمركبات المحضره في هذا البحث فقد تم استخدام برنامج الحاسوب المعروف بأ سم (Alchemy 2000 version 1) ، حيث اظهرت البنيه الهندسيه الامثل لهذه المركبات انها تمتلك الخطيه اللازمه لظهور الاطوار البلوريه السائله و كذلك الحصول على عزم ثنائي القطب الكهربائي لهذه المركبات ، حيث كانت قيمة هذا العزم تتراوح بين (0.7565 - 3.7547 ديباي) للمركبات المختلفه.