World Journal of Environmental Biosciences

Available Online at: **www.environmentaljournals.org**

Volume7, Issue 3: 108-111

ISSN 2277- 8047

Synthesis and Characterization and Studying Liquid Crystal Properties of Some Schiff Base Compounds Substituted with Aliphatic Long Chain

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ABSTRACT

This research included the synthesis of some schiff bases including S_1-S_5, and S_6-S_8 with liquid crystal properties. The prepared compounds were diagnosed by spectroscopy methods including FTIR and ^{1}H-NMR. The results of FTIR, they were similar to the literature. The liquid crystalline state of the synthesized compounds (S_5, S_7, and S_8) was obtained in nematic phase, and the changes were observed at different temperatures, It was confirmed that there were transitions in phases by using Differential Scanning Calorimeter (DSC). The purity of the synthesized compounds was checked by thin layer chromatography (TLC), and the melting point of the purified schiff base was also measured.

Keywords: *Schiff base, Mesogen, Mesomorphic, Nematic.*

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Received: 12 January 2018
Accepted: 30 April 2018

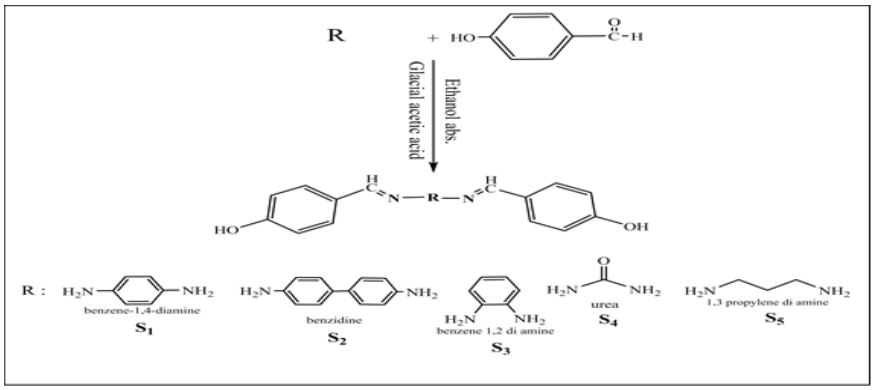
1. INTRODUCTION

Schiff bases, which were first discovered in 1864 by Hugo Schiff, are condensation products of carbonyl compounds and primary amines (Ashraf et al., 2011). They are analogs of a ketone or aldehyde, in which the carbonyl group (C=O) has been substituted by an imine or azomethine group (Kalaivani et al., 2012). Typical terminal parts showing liquid crystal properties are those azomethine group. Polar substituents have strong dipole moments, thus are able to promote mesomorphic properties (Galewski et al., 1999). The enhanced dipole moment increases the stability of the lattice and melting temperatures (Galewski Z, 1994). With the increase of the terminal substituent's length, the molecules tend to have a parallel orientation (Dave et al., 2000). The nature of the central core, linking groups, and lateral substituents lead to a significant impact on the mesophase morphology as well as physical characteristics of calamitic LCs (Ha et al., 2013). The nematic phase derives its name from a Greek word nematos, which denotes something thread-like in shape. Molecules in the nematic phase have long-range orientation order, but no positional order (Demus et al., 2008) Chiral molecules can also form a nematic phase which is called a chiral nematic or cholesteric (N*) phase when the sample is made up of chiral atom/atoms, or it is doped with chiral molecules. In this phase, the molecules are arranged in a nematic order in layers represented by their directors and those nematic layers with their directors rotating constantly from layer to layer around the helical axis (Chen et al., 2013) The smectic phase derives its name from Greek word smectos, which means soap-like, the smectic phase is more ordered then the nematic phase (Collings et al., 1997).

2. EXPERIMENTAL

2.1. Preparing Schiff base compounds of S_1 - S_5

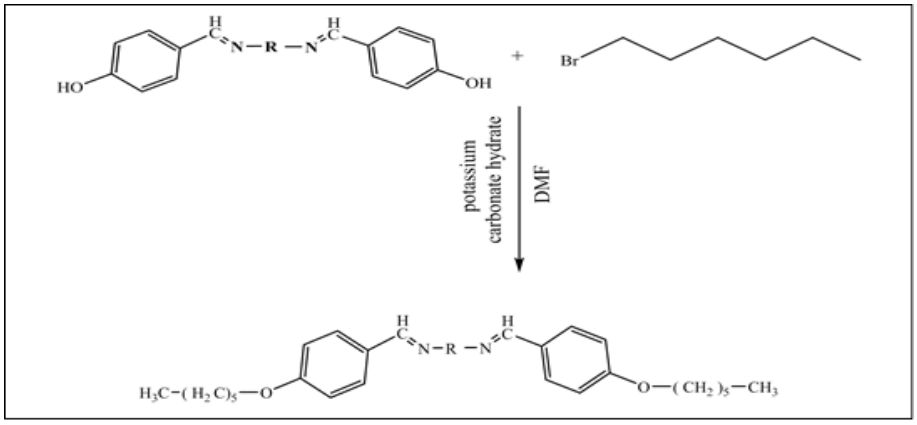
For synthesis of Schiff base, 10 ml of an ethanolic solution of p-Phenylenediamine (0.324 g - 0.003 mol) was added to 10 ml of an ethanolic solution of O-hydroxybenzaldehyde (0.636 g – 0.006 mol) with few drops of glacial acetic acid. The mixture was refluxed for 4hrs, the solvent was removed, and the solid product was collected from ethanol and crystallized (Noor Sabah et al., 2018).



Scheme 1. The general equation for preparation of series of Schiff compounds (S_1 – S_5).

2.2. Preparing Schiff base compounds of S_6 – S_8

0.001 mol of S_1, S_2, and S_4 were dissolved in 15 ml of DMF, then 0.01 mol of potassium carbonate hydrate was added and stirred with stirrer for 30 min. After that, 0.02 mol of 1-bromohexane was added drop by drop on a stirrer. The mixture was refluxed for 10-12 hrs, filtered and extracted by using water and ethyl acetate. Finally, the precipitate was collected, and the yield was calculated (Noor et al 2018).



Scheme 2. The general equation for preparation series compounds of Schiff base (S_6 – S_8).

3. RESULTS AND DISCUSSION

3.1. Spectroscopic studies

3.1.1. Spectroscopic study by IR spectrum

The infrared spectrophotometer technique was used to characterize the synthesized compounds. It showed vibration (stretching and bending) of new functional group which was produced after chemical reaction. The infrared spectrum of S_1 showed absorption bands at 3232 cm^{-1} attributed to stretching vibration of υ (O – H) group; the band appeared at 3034.6 cm^{-1} was attributed to stretching vibration of υ (C – H aromatic); the band appeared at 1669 cm^{-1} was attributed to stretching vibration of υ (C = N) group; the band appeared at (1595.8 cm^{-1}) was attributed to stretching vibration of υ (C = C) group; the band appeared at 1449.5 cm^{-1} was attributed to stretching vibration of υ (- C - O) group; the bands appeared at 1157 and 1219.1 cm^{-1} were attributed to stretching vibration of υ (C – N) group. The IR spectrum showed disappearance of absorption bands υ (NH2) of amine which were used as reactant substance, and also carbonyl group was disappeared. The bands of the synthesized compounds are shown in table 1.

Table 1. Vibration bands of synthesized compounds.

Comp. No.	υ $(cm)^{-1}$, IR						
	O - H	C-H aromatic	C-H Aliphatic	C = N	C=C aromatic	C - O	C – N
S_1	3232	3034.6	--------	1669	1595.8	1449.5	1157 1219.1
S_2	3237.3	3022.4	--------	1668.8	1589	1395	1162.7 1259.7
S_3	3285.9	3008.5	--------	1606.4	1606.4	1457.3	1159.2 1252.8
S_4	3258.1	3029.3	--------	1679.2	1589	1381	1162.7 1252.8
S_5	3210.1	3027.3	--------	1672.6	1595.8	1456.8	1157 1222.8
S_6	--------	3043	2938.2 2865.5	1687.3	1603.6	1312.7	1160 1258.2
S_7	--------	3064	2939.2 2863	1693	1606.4	1308.3	1159.2 1256.3
S_8	--------	3063.9	2939.5 2859	1694.5	1603	1314.2	1164.3 1255.7

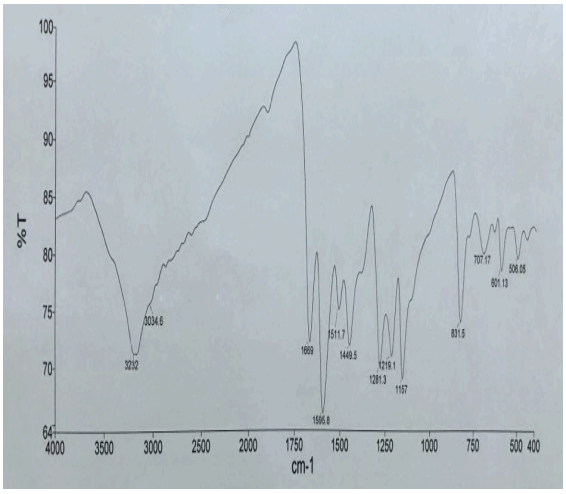


Figure 1. FTIR spectrum of S_1 compound.

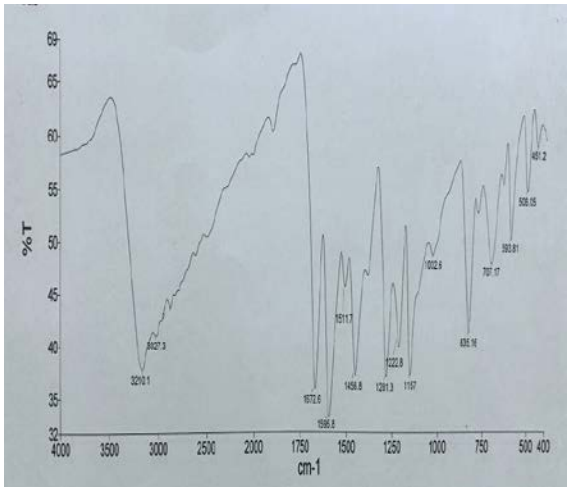


Figure 2. FTIR spectrum of S_5 compound.

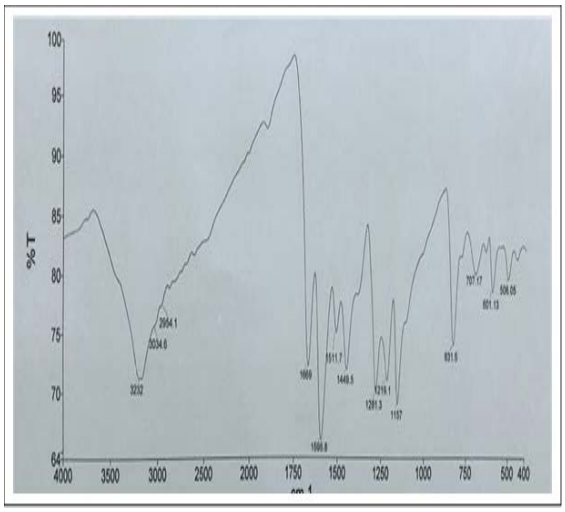


Figure 3. FTIR spectrum of S_8 compound.

3.1.2. Spectroscopic study by ^{1}H-NMR spectrum

^{1}H NMR spectrum (Figure 4): (DMSO-d6, TMS) δ ppm = 5.94-5.96 ppm (d, 4H, arom. H) for the ring, 6.77-6.79 ppm (d, 4H, arom. H) for the ring, 8.31-8.39 ppm (d, 4H, arom. H) for the ring, 8.81 ppm (s, 2 H, imine), 9.80 ppm (s, 2 H, O-H).

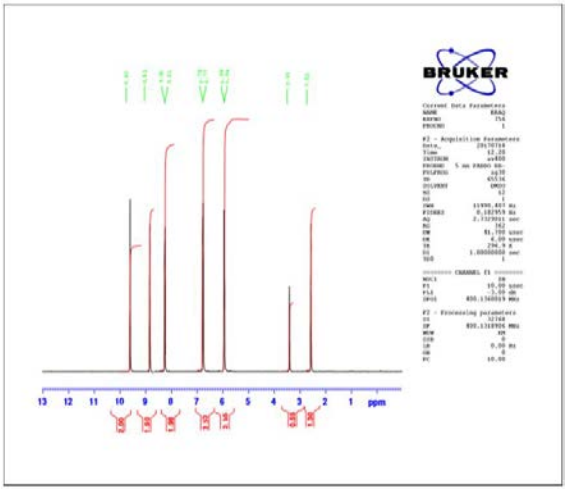


Figure 4. ^{1}H-NMR spectrum of S_1 compound

3.2 Studying of the liquid crystalline state

Liquid crystal properties were studied using hot stage polarized light microscopy. The interpret of moderation phases and the thermal stability is influenced by the nature of the community association in compounds (Marcoset al., 1992). As is known, properties in most of the liquid crystals include being linear, hardness and polarization, and also, the length of the molecule to the diameter rate must be within the range of 4 - 6.4 A. Being linear and hardness in the liquid crystalline phase of these prepared compounds are due to the presence of aggregates phenyl group. The polarization is due to the presence of substituted groups in the rings. The results showed that the ratio of the length of the average diameter within the range known As did (Teucher) and his group (Teucher et al., 1970). Hegee and Vandervee) (Ramamoorthy et al., 2006). showed increased thermal stability because of the increasing polarization of the central molecule as a result of the electrons of double bond, as they form hydrogen bonds within the molecule. Due to several reasons, especially the average diameter of the prepared particles, liquid crystalline phase did not appear for some compounds.

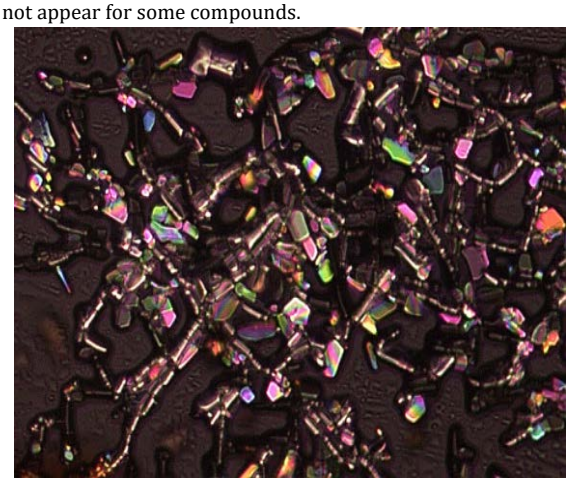


Figure 5. Sample image of S_5 in hot stage polarized light microscopy.

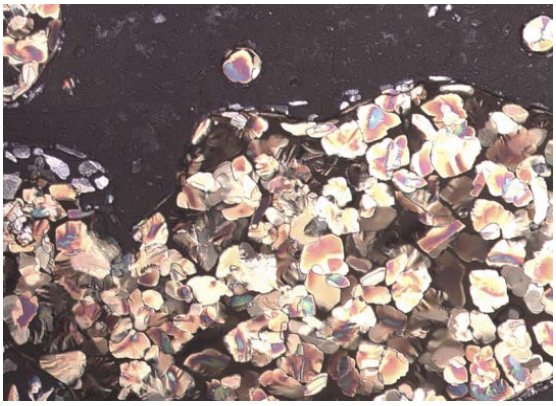


Figure 6. Sample image of S_7 in hot stage polarized light microscopy.

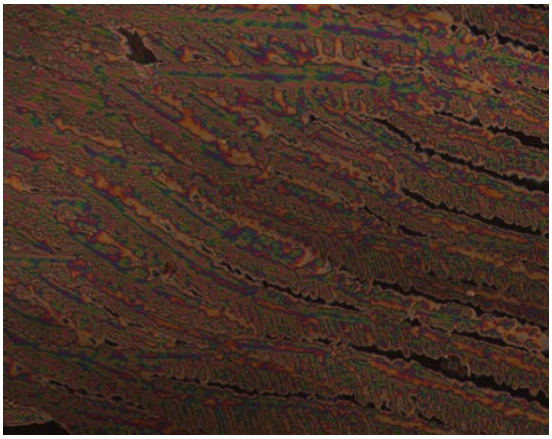


Figure 7. Sample image of S_8 in hot stage polarized light microscopy.

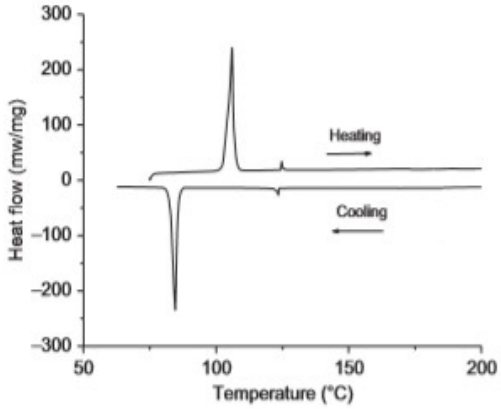


Figure 8. The differential scanning calorimeter thermograms of S_5.

The DSC curve of S_5 showed two endothermic peaks at 105.9, and 124.6 °C which were assigned to the crystal-to-nematic and nematic-toisotropic liquid transitions, respectively. Upon cooling, there were two exothermic peaks that were attributed to the isotropic-to-nematic transition at 123.4 °C and nematic-to-solid transition at 85.5 °C, respectively.

4. CONCLUSIONS

New mesogenic series of schiff base with long chain terminal of aliphatic groups on the central benzene ring were synthesized. The long terminal chain of aliphatic groups is acting as broadening groups on the molecules of S_5, S_7, and S_8 compounds. These groups increase the diameter of the molecule, and change the ratio between the length and diameter of the molecule.

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