

## Synthesis of Mesogenic Compounds and Study the Effect of Terminal groups on their Mesomorphic Properties

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### ABSTRACT

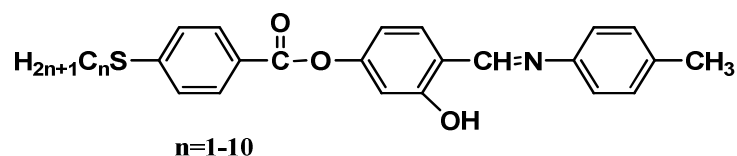
Two long series containing azomethine , esters groups and three aromatic rings with  $\text{CH}_3$  and  $\text{COCH}_3$  on one side of series I and II respectively and thio alkyl group on the other side of both series, have been synthesized and identified by IR ,  $^1\text{H-NMR}$  and elemental analysis. The mesomorphic properties of these compounds were investigated via differential scanning calorimetry and polarizing optical microscopy, and are discussed the effect of length of the thio alkyl and the type of the terminal groups on the mesomorphic properties.

**Keywords:** Schiff base, ester ,Mesogenic properties, Terminal group ,thio alkyl

### INTRODUCTION

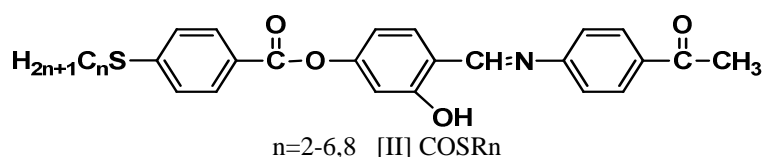
Liquid crystalline behavior of an organic compound is essentially dependent on its molecular structure architecture, in which a slight change in its molecular geometry brings about considerable changes in its mesomorphic properties. Detailed studies by liquid crystal researchers have led to empirical rules , on of which includes the effect of the chemical constitution in the formation of nematogenic and smectogenic mesophases [1].Terminal group of a molecule play an important role in mesomorphic properties of a mesogen.Generally , the terminal substituent's such as alkoxy , alky,l thio alkyl ,cyano and halogens[2,3] of different homologous series with different molecular structures were synthesized by many researchers earlier in order to establish relations between molecular structure and mesomorphic properties [4].Recently ,a large number of studies have been carried out on Schiff base esters duo to their interesting properties[5-8] .

In our work, we have introduced two series of substituted aromatic Schiff bases :



[I] TOSRn

3-hydroxy-4-((p-tolylimino)methyl)phenyl-4-(alkylthio)benzoate



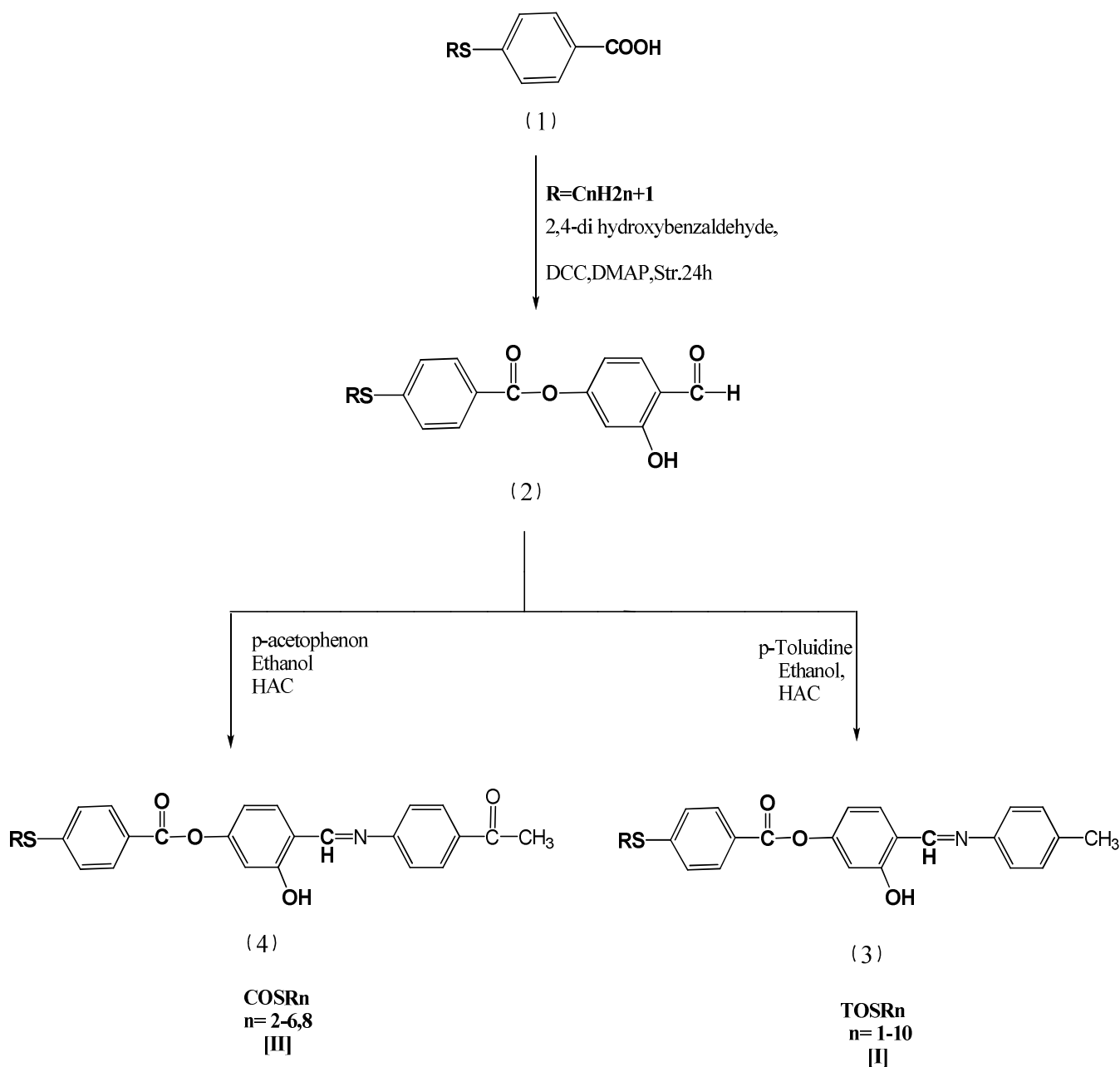
4-(( 4-acetylphenylimino)methyl)-3-hydroxyphenol-4-(alkylthio)benzoate

Our intention is to describe the mesomorphic properties observed in relation to the molecular structure of these Schiff bases and paying special attention to effect of the length of the terminal thioalkyl on one side of the chain and the type of substituent on the other side on the mesomorphic properties.

### MATERIALS AND METHODS

These compounds were characterized by elemental analysis, infrared spectral data and  $^1\text{H}$  NMR spectral data. Infrared spectra were recorded as KBr pellets on a Buck – M500 spectrometer.  $^1\text{H}$ -NMR spectra were recorded on Bruker – 300 using  $\text{CDCl}_3$  as a solvent. Elemental analysis was performed on Euro Vectro EA 3000A.

The phase transitions were observed with a Leitz Laborlux 12 Pol optical microscope with polarized light in conjunction with a leitz 350 hot stage equipped with a Vario – Orthomat camera of transition temperatures were made using a Shimadzu 24 DSC – 50 differential scanning calorimeter with a heating rate of  $10^\circ\text{C min}^{-1}$ .



Scheme 1: Synthesis steps of prepared compounds in series I and II

**Procedure for synthesis of compounds****Synthesis of thioalkyl benzoic acid (1)**

Solutions of 4-mercapto benzoic acid (10mmol) in dry ethanol (50ml) and of KOH (20mmol) in dry ethanol (50ml) were magnetically stirred with simultaneous drop-wise addition of 1-bromo alkane (10mmol) the reaction mixture was refluxed for 24h and allowed to come to room temperature. The alkoxy potassium salts thus obtained were separated out by filtration under suction and treated with dilute HCl until the pH of the reaction mixture reached ~2. The crude solid white product was filtered off, washed thoroughly with water and recrystallized successively from solution of ethanol [9]. (Scheme 1)

**Synthesis of esters (2)**

Esters were synthesized by a modification of a literature method [10]. (Scheme 1)

**Synthesis of Schiff bases (3 and 4)**

Absolute ethanolic solution (10 mmol) of ester for the prepared compound (2) and (10 mmol) of toluidine and para amino acetophenone to get series I and series II respectively. The mixtures were stirred for 2 hours after the addition of a few drops of acetic acid and the resultant solutions were left at room temperature [11]. The micro-crystalline yellowish colored products were filtered and washed with ethanol and recrystallized from hexane. (Scheme 1)

**RESULTS AND DISCUSSION****Characterization**

The presented compounds (series I and II) were characterized by elemental analysis and various spectroscopic methods, <sup>1</sup>H-NMR and IR. The elemental analysis of the compounds **TOSR**<sub>1,2,4,6,7,8,10</sub> and **COSR**<sub>2,3,5,8</sub> are consistent with their proposed structures (table 1 and 2)

**Table 1: Elemental analytical data (calculated value in parentheses) and the most relevant IR data for compounds in series I**

Compound	Molecular Formula	%C	%H	%N	%S	C=O cm <sup>-1</sup> Ester	CH=N cm <sup>-1</sup>
<b>TOSR</b> <sub>1</sub>	C <sub>22</sub> H <sub>19</sub> O <sub>3</sub> NS	70.02 (70.32)	5.03 (5.04)	3.71 (3.82)	8.48 (8.53)	1730	1622
<b>TOSR</b> <sub>2</sub>	C <sub>23</sub> H <sub>21</sub> O <sub>3</sub> NS	70.58 (70.32)	5.37 (5.31)	3.58 (3.39)	8.18 (8.37)	1730	1622
<b>TOSR</b> <sub>4</sub>	C <sub>25</sub> H <sub>25</sub> O <sub>3</sub> NS	71.59 (71.24)	5.96 (6.04)	3.34 (3.39)	7.63 (7.68)	1730	1622
<b>TOSR</b> <sub>6</sub>	C <sub>27</sub> H <sub>29</sub> O <sub>3</sub> NS	72.48 (72.00)	6.48 (6.41)	3.05 (3.01)	7.15 (7.17)	1731	1620
<b>TOSR</b> <sub>7</sub>	C <sub>28</sub> H <sub>31</sub> O <sub>3</sub> NS	72.88 (72.55)	6.72 (6.78)	3.03 (3.14)	6.94 (6.83)	1730	1622
<b>TOSR</b> <sub>8</sub>	C <sub>29</sub> H <sub>33</sub> O <sub>3</sub> NS	73.26 (73.49)	6.94 (6.94)	2.94 (2.19)	6.73 (6.70)	1730	1622
<b>TOSR</b> <sub>10</sub>	C <sub>31</sub> H <sub>37</sub> O <sub>3</sub> NS	73.95 (73.43)	7.35 (7.27)	2.78 (2.73)	6.36 (6.39)	1730	1623

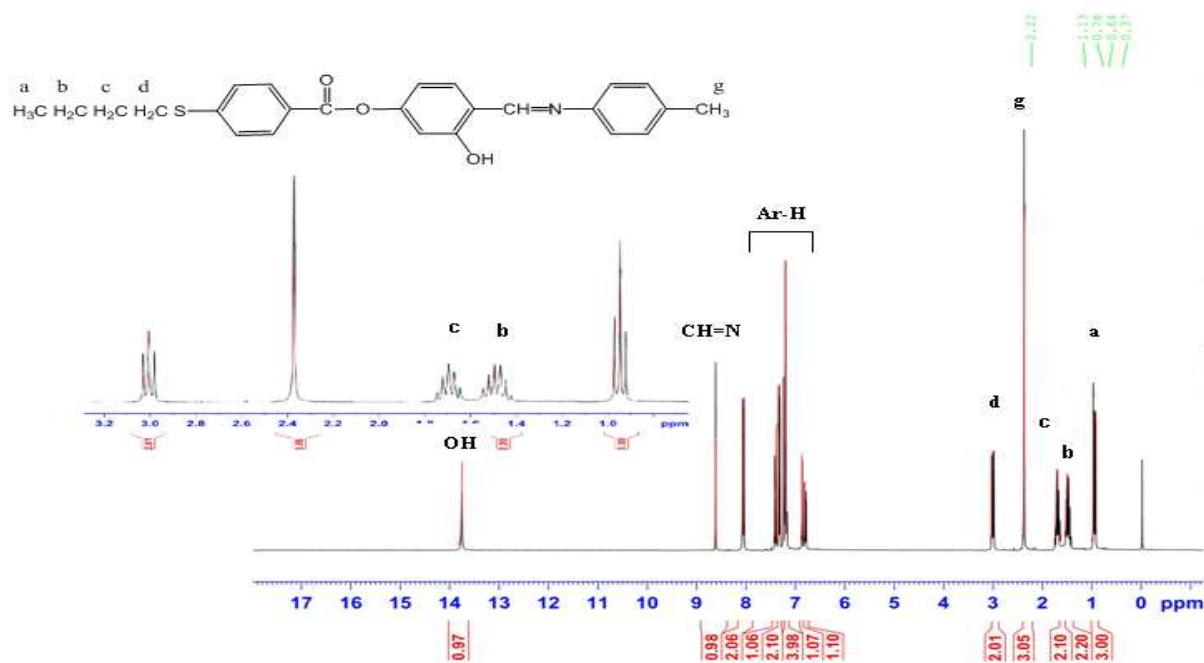
**Table 2: Elemental analytical data (calculated value in parentheses) and the most relevant IR data for compounds in series II**

Compound	Molecular Formula	%C	%H	%N	%S	C=O cm <sup>-1</sup> Ester	C=O cm <sup>-1</sup> Ketone	CH=N cm <sup>-1</sup>
<b>COSR</b> <sub>2</sub>	C <sub>24</sub> H <sub>21</sub> O <sub>4</sub> NS	68.73 (68.42)	5.01 (5.09)	3.34 (3.31)	7.63 (7.74)	1730	1674	1625
<b>COSR</b> <sub>3</sub>	C <sub>25</sub> H <sub>23</sub> O <sub>4</sub> NS	69.28 (70.55)	5.31 (5.21)	3.23 (3.27)	7.39 (7.27)	1730	1674	1625
<b>COSR</b> <sub>5</sub>	C <sub>27</sub> H <sub>27</sub> O <sub>4</sub> NS	70.28 (70.42)	5.85 (5.77)	3.03 (3.07)	6.94 (6.92)	1730	1674	1625
<b>COSR</b> <sub>8</sub>	C <sub>30</sub> H <sub>33</sub> O <sub>4</sub> NS	71.57 (71.37)	6.56 (6.51)	2.78 (2.67)	6.36 (6.25)	1730	1674	1625

The <sup>1</sup>H-NMR data of the compounds in series I and II give definite evidence for the molecular structures (Table 3 and 4, Figure 5 and 6).

Table 3 : <sup>1</sup>H-NMR data for compounds in series I (ppm)

Compound	OH	CH=N	Aromatic protons	Aliphatic protons
TOSR <sub>1</sub>	13.60 (S,1H)	8.62 (S, 1H)	6.79-8.02 (m,11H)	2.54 (S, 3H,CH <sub>3</sub> ), 3.10 (S, 3H,CH <sub>3</sub> )
TOSR <sub>2</sub>	13.80 (S,1H)	8.62 (S, 1H)	6.79-8.09 (m,11H)	1.38 (t, 3H, CH <sub>3</sub> ), 2.38(S, 3H, CH <sub>3</sub> ), 3.02(q, 2H,SCH <sub>2</sub> )
TOSR <sub>3</sub>	13.80 (S,1H)	8.62 (S,1H)	6.78 – 8.09 (m, 11H)	1.15(t, 3H, CH <sub>3</sub> ), 1.74 (Sex, 2H, CH <sub>2</sub> ), 2.37(S, 3H,CH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
TOSR <sub>4</sub>	13.80 (S, 1H)	8.62 (S, 1H)	6.78 – 8.09 (m,11H)	0.78(t, 3H, CH <sub>3</sub> ), 1.49(Sex, 2H, CH <sub>2</sub> ), 1.70 (P, 2H, CH <sub>2</sub> ), 2.36(S, 3H, CH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
TOSR <sub>5</sub>	13.80 (S,1H)	8.62 (S,1H)	6.78–8.07 (m, 11H)	0.87 (t, 3H, CH <sub>3</sub> ), 1.45 (Hextet, 2H, CH <sub>2</sub> ), 1.71(p, 2H, CH <sub>2</sub> ), 2.37(S, 3H, CH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
TOSR <sub>8</sub>	13.75 (S, 1H)	8.62 (S,1H)	6.78 – 8.07 (m,11H )	0.87(t, 3H, CH <sub>3</sub> ), 1.28–1.47 (m, 8H, (CH <sub>2</sub> ) <sub>4</sub> ), 1.46(P, 2H, CH <sub>2</sub> ), 1.71(P, 2H, CH <sub>2</sub> ), 2.37(S, 3H, CH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
TOSR <sub>9</sub>	13.80 (S,1H)	8.62 (S,1H)	6.78–8.07 (m, 11H)	0.87 (t, 3H, CH <sub>3</sub> ), 1.20-1.50(m, 8H, (CH <sub>2</sub> ) <sub>5</sub> ), 1.45(p, 2H, CH <sub>2</sub> ), 1.70(p, 2H, CH <sub>2</sub> ), 2.37(S, 3H, CH <sub>3</sub> ), 3.00 (t, 2H, SCH <sub>2</sub> ), ,
TOSR <sub>10</sub>	13.80 (S,1H)	8.62 (S,1H)	6.78–8.07 (m, 11H)	0.87 (t, 3H, CH <sub>3</sub> ), 1.20-1.50(m, 8H, (CH <sub>2</sub> ) <sub>6</sub> ), 1.45(p, 2H, CH <sub>2</sub> ), 1.45(p, 2H, CH <sub>2</sub> ) , 2.37(S, 3H, CH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )

Figure 5: <sup>1</sup>H-NMR for TOSR<sub>4</sub> with expansion for aliphatic protonsTable 4: <sup>1</sup>H-NMR data for compounds in series II (ppm)

Compound	OH	CH=N	Aromatic protons	Aliphatic protons
COSR <sub>2</sub>	13.30(S,1H)	8.62(S,1H)	6.86 – 8.12 (m, 11H)	0.95 (t, 3H, CH <sub>3</sub> ), 2.60(S, 3H, COCH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
COSR <sub>3</sub>	13.80(S,1H)	8.62(S,1H)	6.78–8.09 (m, 11H)	1.15 (t, 3H, CH <sub>3</sub> ), 1.74(Sextet, 2H, CH <sub>2</sub> ), 2.37(S, 3H, COCH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
COSR <sub>4</sub>	13.20(S,1H)	8.62(S,1H)	6.82 – 8.09 (m, 11H)	0.95 (t, 3H, CH <sub>3</sub> ), 1.49(Sextet, 2H, CH <sub>2</sub> ), 1.70(P, 2H, CH <sub>2</sub> ), 2.60 (S, 3H, COCH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
COSR <sub>5</sub>	13.3(S,1H)	8.62(S,1H)	6.80–8.12 (m, 11H)	0.96 (t, 3H, CH <sub>3</sub> ), 1.30-1.41(m, 4H, (CH <sub>2</sub> ) <sub>2</sub> ), 1.70(p, 2H, CH <sub>2</sub> ), 2.60 (S, 3H, COCH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
COSR <sub>6</sub>	13.80(S,1H)	8.62(S,1H)	6.78–8.07 (m, 11H)	0.87 (t, 3H, CH <sub>3</sub> ), 1.20-1.50(m, 4H, (CH <sub>2</sub> ) <sub>2</sub> ), 1.45(p, 2H, CH <sub>2</sub> ), 1.72(p, 2H, CH <sub>2</sub> ), 2.37(S, 3H, CH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )
COSR <sub>8</sub>	13.21(S,1H)	8.62(S,1H)	6.80–8.06 (m, 11H)	0.87 (t, 3H, CH <sub>3</sub> ), 1.28(m, 8H, (CH <sub>2</sub> ) <sub>4</sub> ), 1.66(p, 2H, CH <sub>2</sub> ), 1.73(p, 2H, CH <sub>2</sub> ), 2.61(S, 3H, COCH <sub>3</sub> ), 3.00(t, 2H, SCH <sub>2</sub> )

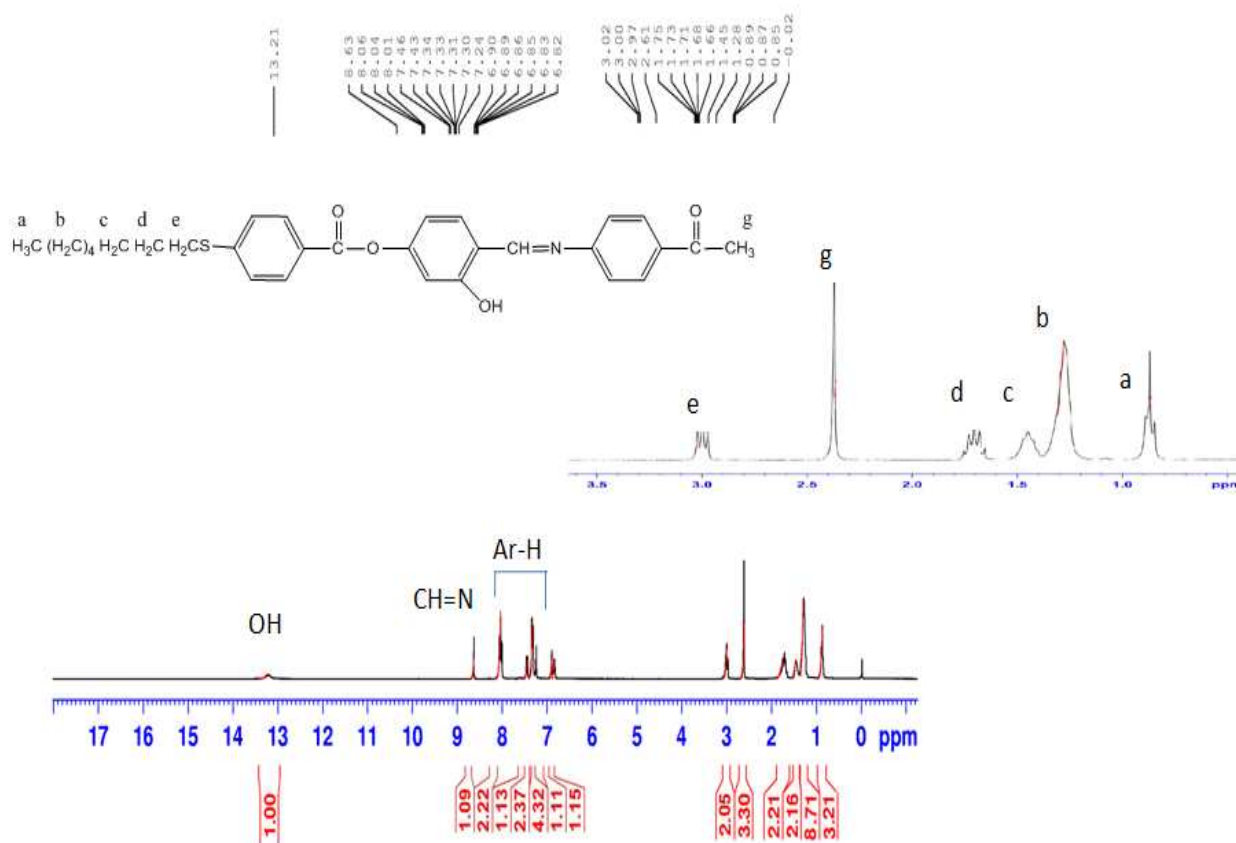


Figure 6: <sup>1</sup>H-NMR for COSR<sub>8</sub> with expansion for aliphatic protons

### Mesogenic behavior

The mesogenic properties of the prepared compounds were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). DSC thermograms of the compounds were measured by heating rate was 10 °C/min. The phase transition temperatures of the compounds are summarized in table 5 and 6. The tables shows that all synthesized Schiff bases exhibit mesogenic behavior.

Table 5. The phase transitions temperatures (°C) of series [1] and associated enthalpy data (kJ/mol) in parentheses

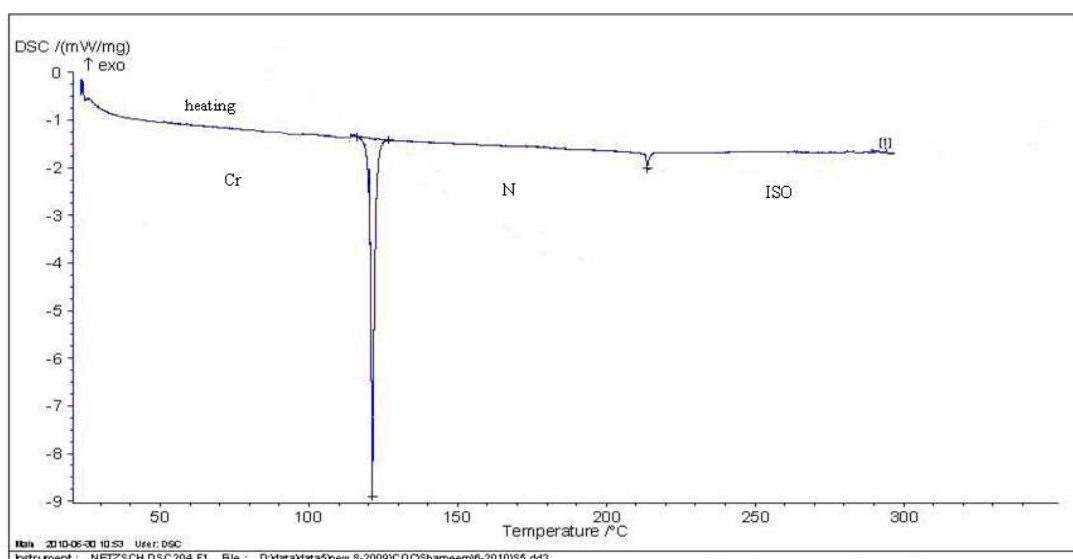
Compound	Phases		ΔT <sub>N</sub>
	Transition	Temperatures °C	
TOSR <sub>1</sub>	C-N	120.0(25.73)	120.0
	N-I	240.0 (2.44)	
TOSR <sub>2</sub>	C-N	118.0 (26.69)	115.0
	N-I	233.0(1.94)	
TOSR <sub>3</sub>	C-N	116.9(36.38)	107.8
	N-I	224.7(1.70)	
TOSR <sub>4</sub>	C-N	127.9(39.14)	94.1
	N-I	222.0(1.44)	
TOSR <sub>5</sub>	C-N	121.4(29.56)	92.3
	N-I	213.7(1.21)	
TOSR <sub>6</sub>	C-N	119.8(39.95)	89.1
	N-I	208.9(1.59)	
TOSR <sub>7</sub>	C-N	114.7(43.54)	84.9
	N-I	199.6(1.72)	
TOSR <sub>8</sub>	C-N	117.2(14.82)	78.4
	N-I	195.6(2.27)	
TOSR <sub>9</sub>	C-N	107.4(29.46)	76.0
	N-I	183.4(2.37)	
TOSR <sub>10</sub>	C-N	116.9(44.75)	63.2
	N-I	180.1(2.88)	

Cr: Crystals, N: Nematic, Iso: Isotropic, ΔT<sub>N</sub> Nematic thermal range

The mesogenic Schiff bases (series I and II) have high molecular lengths coupled with extension of the conjugation through the ester linker and azomethine group, this increases the electronic polarizability of the molecule. These two effects cause an increase in the anisotropy of the polarizability of molecules with three aromatic rings, that enhance the molecular interactions and then liquid- crystalline properties[1,12].

In series I all the compounds showed Nematic phase only (table.5, figure.1), The larger size of sulfur atom prevents the alkyl chains from getting as close together as they do in the compounds which substituted with alkoxy chain[13], this cause a reduction in their mutual interactions and , consequently, lowering the melting points , this reason makes it difficult for the molecules to be gathered to form more organized liquid crystalline phase (Smectic phase ).

The compounds which have the similar molecular structures[14] to our compounds substituted with alkoxy group(OR) exhibit smectic and nematic phases in compared to our compounds which are substituted with thio alkyl group (SR) exhibit only Nematic phase .That could be explained as a result to the bigger size of sulfur atom[13].



Cr:Crystals , N:Nematic, Iso: Isotropic

Figure 1. DSC thermogram of TOSR<sub>5</sub> during heating cycle

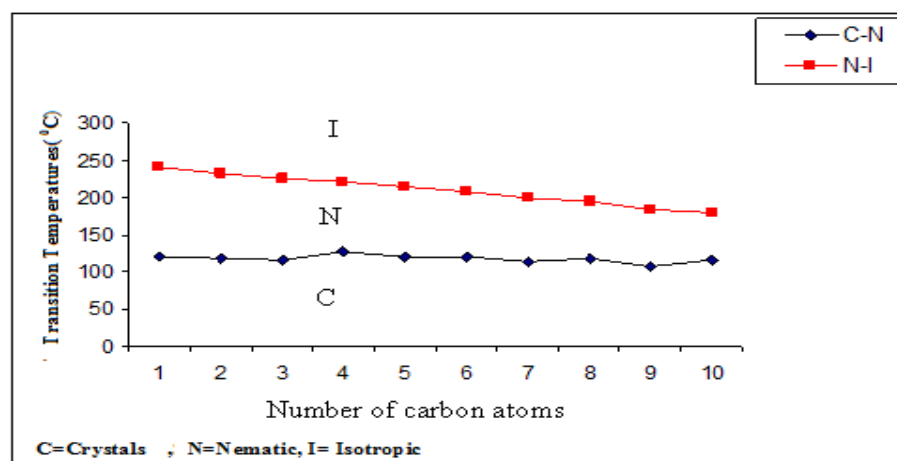


Figure 2. Phase transition temperatures as a function of the thioalkyl chain length for series [I].

The lowering of the nematic –isotropic transitions temperatures and the thermal stability of Nematic phase with an increase in the length of thio alkyl chain could be explained by the length of the alkyl chain affects on the length to width ratio in the mesogen ,as the length of the alkyl chain increases , the lateral attraction increases

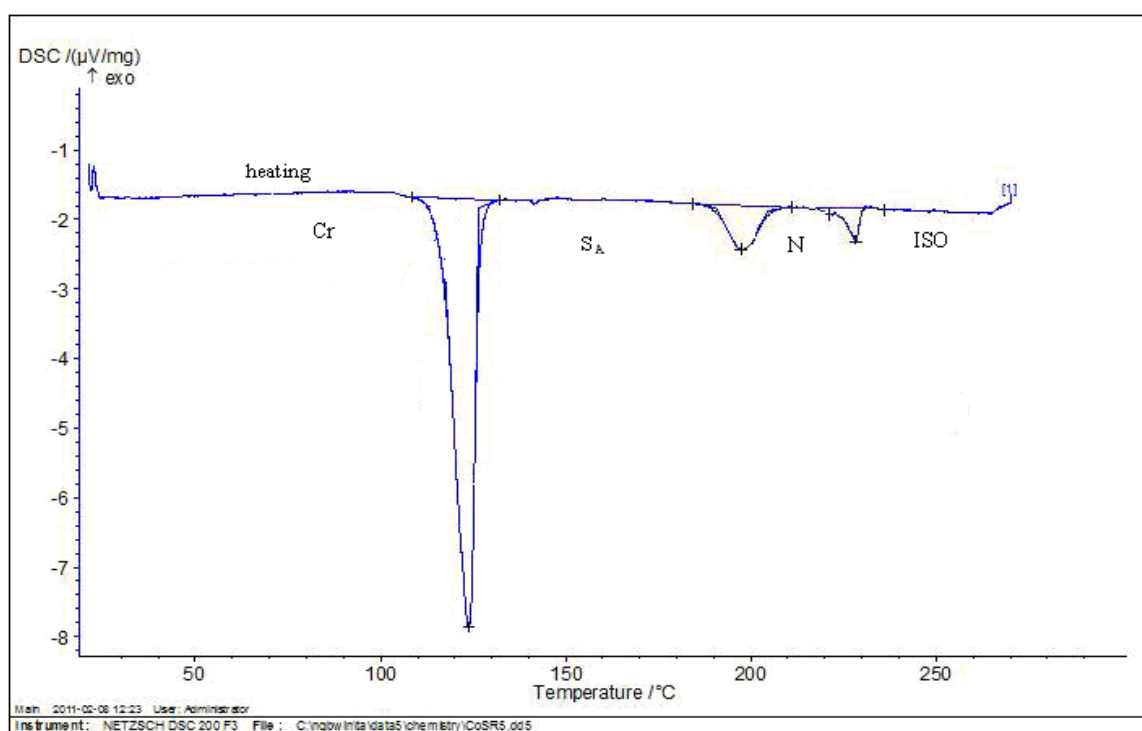
too<sup>[15]</sup>. However, the terminal attraction becomes relatively weaker as the flexibility of the molecule increases, which causes a reduction in the Nematic phase stability [15] as shown in Figure 2.

In series II, however, all the compounds are mesomorphic and the type of mesophase depends on the length of the terminal chain (table.6 and figure 1). A Nematic phase was found for the terminal chain  $n=2$ . When the terminal chains had  $n=3,4,5$ , the compounds presented Smectic A as well as Nematic phase. Finally, for the longest chains  $n=6$  and  $8$ , only Smectic A phases are observed.

Table 6. The phase transitions temperatures(°C) of series[II] and associated enthalpy data (kJ/mol) in parentheses

Compound	Phases		$\Delta T_S$	$\Delta T_N$
	Transition Temperatures °C			
COSR <sub>2</sub>	C-N	173.2(30.25)	-	67.3
	N-I	240.5(2.61)		
COSR <sub>3</sub>	C-S	144.1(32.80)	55.9	37.0
	S-N	200.0(1.35)		
	N-I	237.0(1.21)		
COSR <sub>4</sub>	C-S	139.0(34.10)	64.0	27.0
	S-N	203.0(1.60)		
	N-I	230.0(1.59)		
COSR <sub>5</sub>	C-S	123.7(36.23)	78.3	26.0
	S-N	202.0(2.72)		
	N-I	228.0(2.27)		
COSR <sub>6</sub>	C-S	135.0(38.28)	88.0	-
	S-I	223.0(2.81)		
COSR <sub>8</sub>	C-S	119.4(40.45)	104.4	-
	S-I	223.8(2.91)		

Cr: Crystals, N: Nematic, S<sub>A</sub>: Smectic A, Iso: Isotropic,  $\Delta T_S$ : Smectic thermal range  $\Delta T_N$ : Nematic thermal range



Cr: Crystals, S<sub>A</sub>: Smectic A, N: Nematic, Iso: Isotropic

Figure 3. DSC thermogram of COSR<sub>5</sub> during heating cycle

The difference between series[I] and series [II] can be attributed to the carbonyl group at the terminal of molecule which have dipole moment across the long axis of molecule and this type of dipole moment enhance the lateral attraction forces between the side ends of the molecules and then enhances the Smectic (S<sub>A</sub>) phase to appear in the compounds of series II[16].

Under polarizing optical microscopic the Nematic phase reflects the marbled texture on heating and the Schlieren texture on cooling. The Smectic( $S_A$ ) phase was clearly characterized by its typical focal conic textures texture in heating and bâtonnets in cooling(Fig.4).

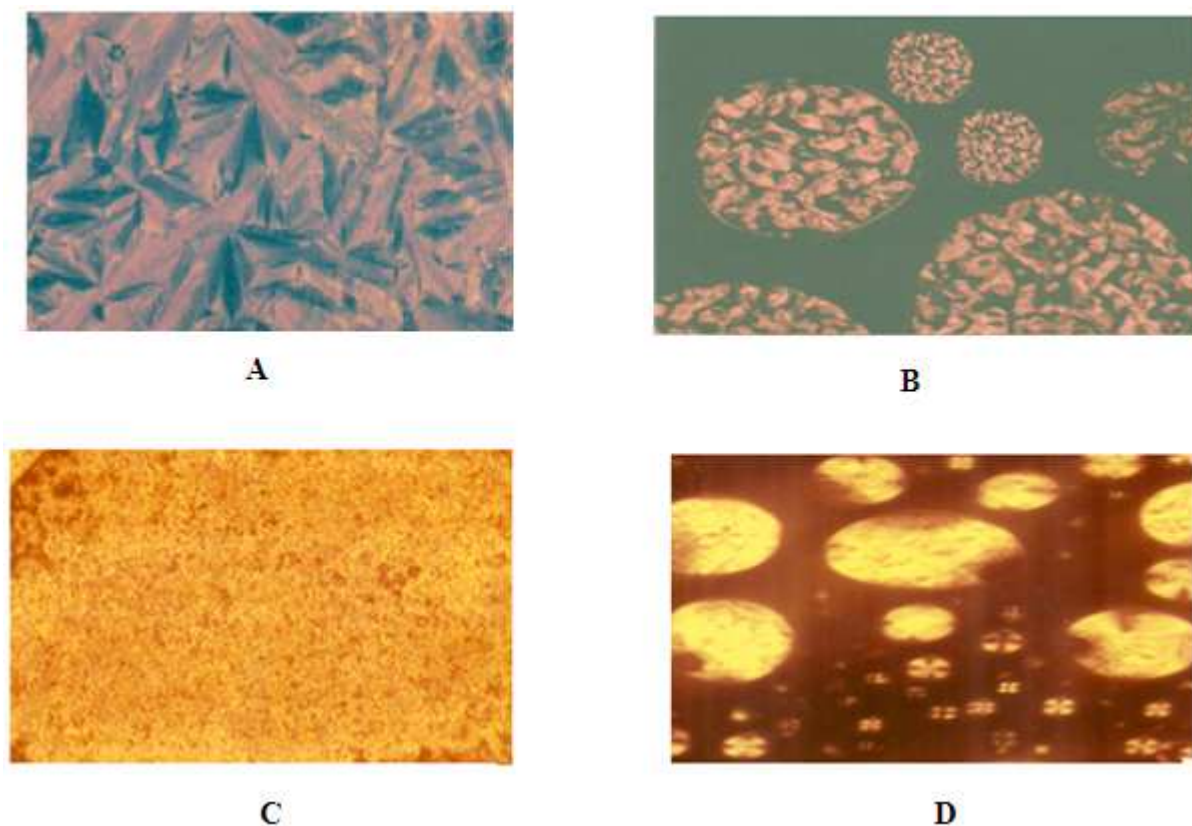


Figure 4. A.: focal conic texture of the smectic A in heating of COSR<sub>3</sub>, B: bâtonnets texture for smectic A phase in cooling for COSR<sub>3</sub>, C:Marble texture for Nematic phase in heating for TOSR<sub>1</sub>, D: Marble texture for Nematic phase at the beginning of melting point for TOSR<sub>1</sub>,E. Schlieren texture for Nematic phase in cooling for TOSR<sub>1</sub>

### CONCLUSION

New Schiff bases mesogenic compounds with thioalkyl group were synthesized. The study indicated that the change in the length and type of terminal groups effect on the mesomorphic properties of the mesogenic compounds.

### REFERENCES

- [1] G.W. Gray. *molecular structure and the properties of liquid crystals*, 2nd ed; academic press, London. **1962**.
- [2] G. Yeap, H.T.L. Lim, p.Boey. *Liquid crystals*. **2006a**, 33,2,205-211.
- [3] H.T. Sie, L. Ong, J.Wong, Y.Yeap, H.Lin, S.Ong and. *phase transition*. **2009**, 82, 387-397.
- [4] H. Kelker, B. Scheurie, A. Angew. *Chem.Int.Edn.* **1969**, 8, 884-885.
- [5] P.M.; J.Zuniga, C.Soto, E.Sierra, T; Serrano, J. *Liq.Cryst.* **2004**, 32, 457-462
- [6] G.Y. Yeap, S. Ha, P.Lim., L.Boey, P.Mahmood, W. Itos, M. Sanehisa *Mol.Cryst.Liq.Cryst.* **2004**, 423, 73-84.
- [7] B. Eran; A. Nesrullajev, N.Canli. *Mat.Chem.Phys.* **2008**, 111, 555-558.
- [8] H.T. Sie, L. Ong, k. Sivasothy, Y. Yeap, G. Lin, H. Lee, S.Boey, P. Bonde. *International Journal of the Physical Sciences*. **2010**, 5, 564-575.
- [9] E. Campillos, M. Marcose, J. Serrano. *J.Mater.Chem.* **1993**, 3, 1049-1052.
- [10] U.J. Al-Hamdani, E. Tarik, H. Hamed. *Molecules*. **2010**, 15, 5620-5628.
- [11] H.T. Sie, Y. Guan. *Australian Journal of Basic and Applied Sciences*. **2009**, 3, 3417-3422.
- [12] E. Smits, J. Engberts. *Mol.Cryst.Liq.Cryst.* **1995**, 260, 185-199.
- [13] U.J. Al-Hamdani. *International Journal of Molecular Science*. **2011**, 12, 3182-3190.
- [14] R.A. Vora, A. Pragapati. *Bull. Mater. Sci.* **2002**, 25, 4, 355-358.
- [15] J.C. Peter, H. Michael. *Introduction to liquid crystals*, 3rd ed; Taylor and Francis, UK and USA. **2004**
- [16] S. Jayrang, M. Meera. *Bull. Mater. Sci.* **2000**, 23, 237-238.