

Article

Mesomorphic Properties of an Homologous Series of Thioalkyl-Terminated Azomesogens

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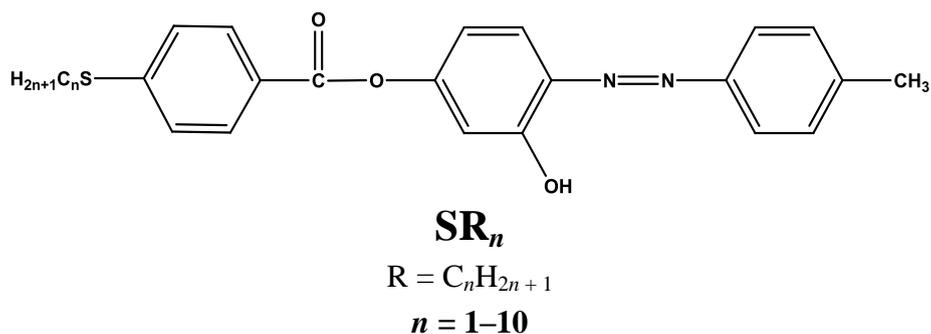
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Abstract: A new homologous series (ten compounds) of 2-hydroxy azo compounds SR_n (where $n:1-10$) were synthesized. Their structures were elucidated using spectroscopic techniques such as IR (Infrared), 1H -NMR as well as elemental analysis. Mesomorphic properties and phase transitions were studied using polarized hot stage optical microscopy and differential scanning calorimetry (DSC), and are discussed as a function of the number of carbon atoms in the thioalkyl chain. It has been found that all compounds in the series are pure nematogens.

Keywords: azo; terminal thioalkyl; Nematic

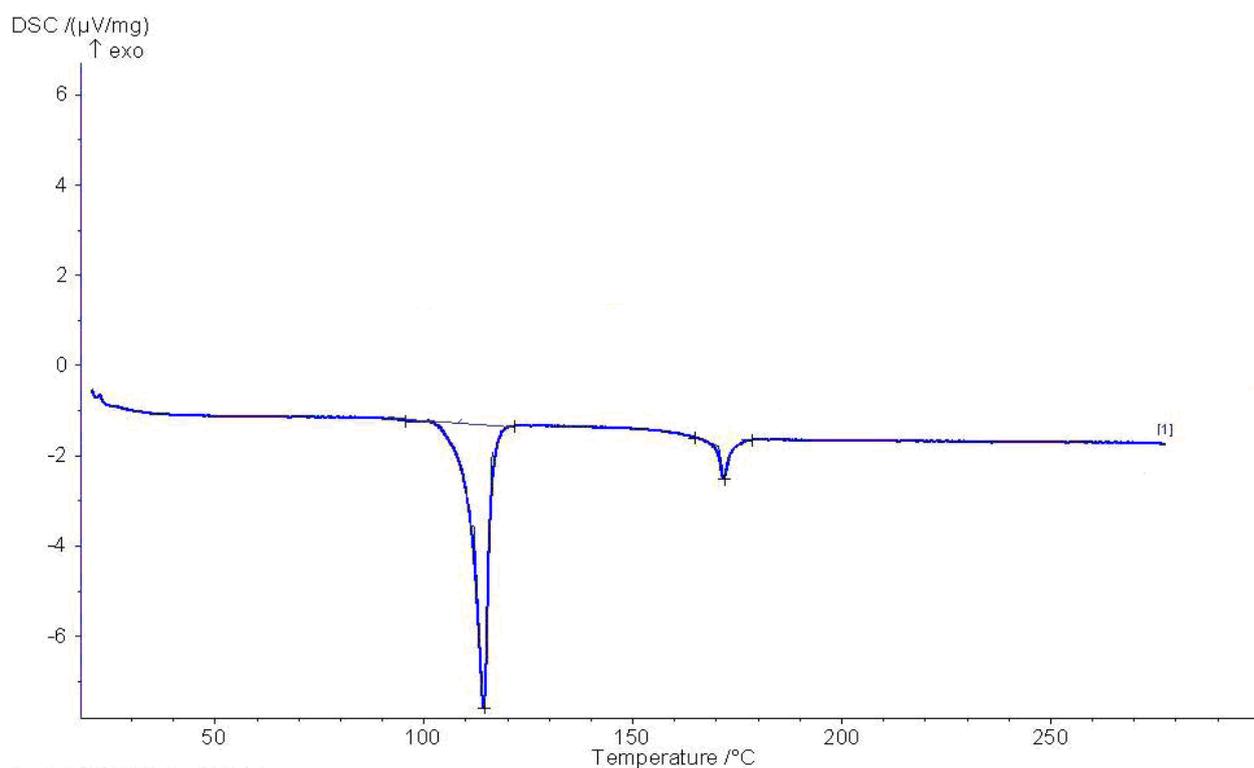
1. Introduction

Liquid crystalline materials are of great interest for materials science as well as for life science. Their properties can be tuned by appropriate molecular design. Thus, it is well known that the mesomorphic properties of calamitic liquid crystals can largely be influenced by the structural variation in terminal substituents, like alkyl, alkyloxy and thioalkyl groups [1–5]. This can influence the melting points and mesophase types, *etc.* [6–10]. Numerous studies have been carried out in recent years of the effects of changes in molecular framework on the incidence and stability of azo ester liquid crystal phase [11–14]. However, a literature survey indicates that liquid crystalline azo esters with thioalkyl chains comprising different kinds of terminal groups are very rare, so, in the present work, we have prepared ten members (Figure 1) of homologous series of (SR_n) in order to establish the effect of introducing sulfur atom instead of oxygen atom with the increase in the terminal thioalkyl chain on liquid crystalline properties.

Figure 1. Structures of the studied compounds SR₁–SR₁₀).

2. Result and Discussion

The DSC scans carried out on these compounds show transitions at temperatures which are in agreement with those obtained by optical microscopy. The phase transition temperatures of all compounds are given in Table 1. All the studied azo compounds exhibit enantiotropic mesogenic behavior. All members of the series show Nematic phase (N) only (Figure 2).

Figure 2. DSC thermogram for E-SR₈.**Table 1.** The phase transitions temperatures (°C) of compounds and associated enthalpy data (kJ/mol, in parentheses).

Compound	C→N	N→I	ΔT_N
SR ₁	123.0 (25.53)	237.0 (1.45)	114.0
SR ₂	118.0 (26.99)	228.0 (1.31)	110.0
SR ₃	114.9 (29.66)	220.7 (1.23)	105.8

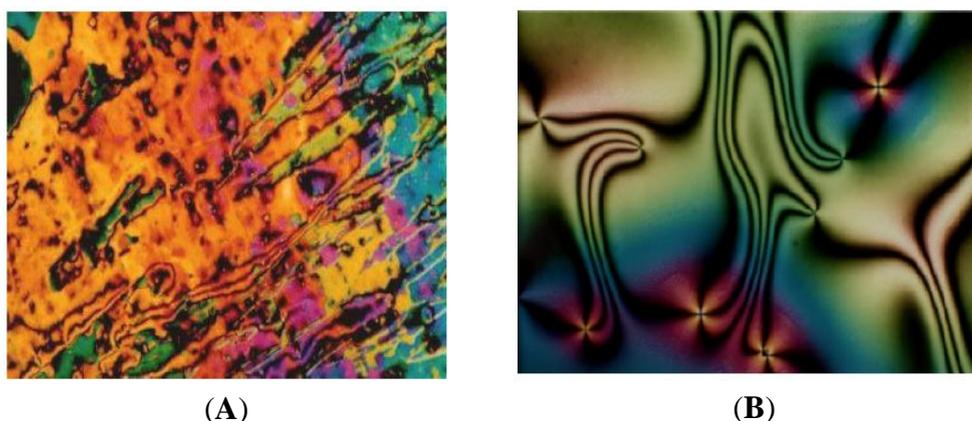
Table 1. Cont.

Compound	C→N	N→I	ΔT_N
SR _{4s}	124.9 (38.14)	220.0 (1.22)	95.10
SR _{5s}	124.4 (39.46)	213.7 (1.11)	89.30
SR _{6s}	117.5 (39.95)	194.9 (1.15)	77.40
SR _{7s}	119.9 (41.85)	189.0 (1.19)	69.10
SR _{8s}	114.5 (42.32)	171.9 (1.16)	57.40
SR _{9s}	115.2 (43.46)	165.0 (0.83)	49.80
SR _{10s}	117.9 (44.75)	160.2 (1.21)	42.30

C = solid; N = Nematic phase; I = Isotropic. ΔT_N : Thermal range of Nematic phase.

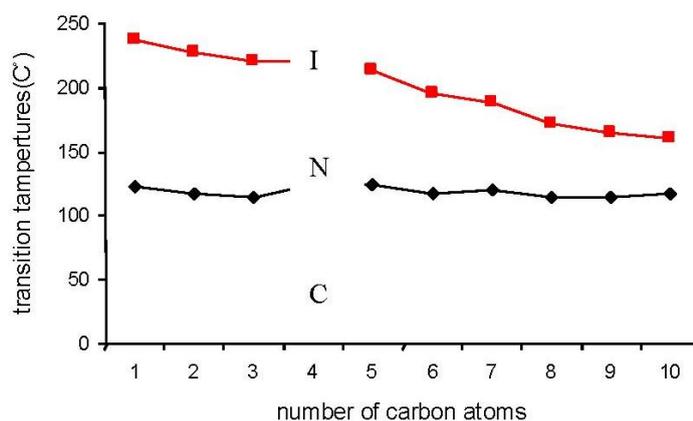
The Nematic phase reflects the marbled texture on heating and the schlieren texture on cooling (Figure 3).

Figure 3. (A) Marble texture for Nematic phase in heating at 150 °C for SR₁; (B) Schlieren texture for Nematic phase in cooling at 234 °C for SR₁.



A plot of transition temperatures against the number of carbon atoms, n , in the thioalkyl chain for the studied compounds (SR _{n}) is given in Figure 4. The plot shows typical mesomorphic trends. The Nematic-isotropic transition temperature curve is a falling one throughout the homologous series. At longer thioalkyl chain lengths, the Nematic phase stability range decreases [15,16].

Figure 4. Phase transition temperatures as a function of the thioalkyl chain length for the SR _{n} series (Black: C→N; Red: N→I; C: Crystalline; N: Nematic; I: Isotropic).



We did not notice the phenomenon of odd–even during the study of the transition temperatures for the prepared compounds. This result coincides with many results from other studies [15,17].

The appearance of this phenomenon in the mesomorphic compounds depends on the molecular structure [5].

Increase in the alkyl chain length should have two effects:

1. Increases the intermolecular attractions between the sides of the molecules, because of the polarizability of each added methylene group;
2. Decreases the intermolecular terminal attractions because of the increasing separation of the molecules containing the dipolar units.

Increase in the alkyl chain length should therefore increase the ratio of the lateral to the terminal attractions between the molecules, so making the probability greater that the layer arrangement will persist after melting when the terminal attractions are weakened. Smectic properties are therefore most likely to be observed in the long chain members of an homologous series of mesomorphic compounds. A common pattern of behavior is that the lower homologous are Nematic, the middle members exhibit a smectic mesophase followed by a nematic and the long chain members are purely smectic. However, our study of the effect of the chain length on the mesomeric properties of the prepared compounds shows the formation of nematic phase only, which indicate that the effect of the terminal attraction forces are higher than the lateral attraction forces which leads to the formation of nematic phase [18,19].

The formation of a high proportion of this kind of attraction forces is due to the presence of sulfur atoms, which are large, and prevent the aggregation of the molecules to form the layer shape and the appearance of the smectic phase. These results were also found in many other studies for compounds which contain sulfur atoms [20]. The compound which have the similar molecular structure with our compounds but substituted by alkyloxy group exhibit the nematic phase as well as smectic phase due to the difference between the oxygen and sulfur in volume [12].

3. Experimental

3.1. General

Infrared spectra were recorded as KBr pellets on a Buck-M500 spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on Gemini-200 using CDCl_3 as a solvent and TMS (TetraMethylSilane $(\text{CH}_3)_4\text{Si}$) as internal standard. 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 $10\text{ }^\circ\text{C min}^{-1}$.

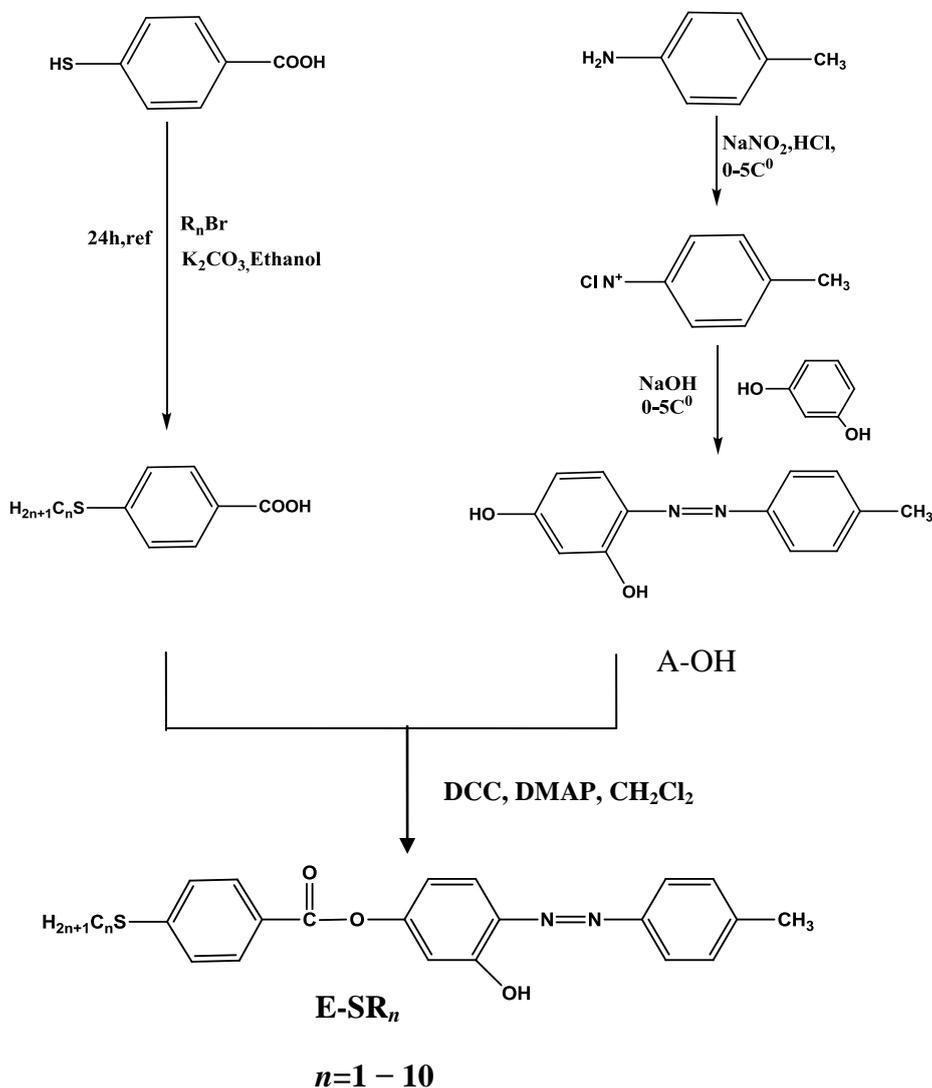
3.2. Synthesis of Azo Compound A-OH

3.2.1. Diazotization of p-Toluidine

A solution of p-Toluidine (10 mmol) in (8 mL 3M HCl) was heated gently, 10 mL of water was added in order to dissolve the solid. The mixture was cooled to $0\text{ }^\circ\text{C}$ in an ice bath with stirring. Some

solid may precipitate, but the reaction will still work well if it is stirred. 10 mL of freshly prepared 1M sodium nitrite solution was then added slowly with stirring. The rate of addition was adjusted so that the temperature of the solutions remained below 10 °C [14]. The solution was kept in an ice bath and proceeds immediately to the next step (Scheme 1).

Scheme 1. Synthesis steps of the prepared compounds.



3.2.2. Coupling with Phenol

A solution of one of the substituted phenol (10 mmol) in 20 mL of 1 M NaOH, was prepared and cooled in an ice bath. The diazonium salt (step 1) then added slowly with stirring to the phenol solution. The reaction mixture then stands in the ice bath for at least 15 minutes until the crystallization is completed (a colored solid). The pH of the solution was adjusted with dilute HCl or NaOH solutions (0.1 M) in order to induce precipitation. The orange azo dye was then collected and washed in cold water [14].

3.3. Synthesis of Esters E-SR_n

Solutions of 4-*n*-thioalkyl benzoic acid (10 mmol), (10 mmol) 1,3-dicyclohexylcarbodiimide (DCC) (55 mmol) in 50 mL dry dichloromethane along with solid 4-dimethyl amino pyridine (DMAP) as catalyst (2.5 mmol) were magnetically stirred at room temperature for 12 h. The byproduct (dicyclohexyl urea) was filtered off under suction and the solvent was removed on rot vapor. The crude product was recrystallized from hot solution of ethanol [21].

4-((4-tolylphenyl)diazenyl)phenol (**A-OH**): yield% 45, m.p.: 192–195 °C, IR cm⁻¹: 3260 (broad OH), 1600 (C=C), Elemental analysis calculated for C₁₃H₁₂O₂N₂: %C 68.42, %H 5.26, %N 12.28. found: %C68.72, %H 5.27, %N 12.33.

3-hydroxy-4-((*p*-tolylidzenyl)methyl)phenyl-4-(methylthio)benzoate (**E-SR₁**): Orange solid; yield% 40; ¹H-NMR (CDCl₃): 2.43 (s, 3H, CH₃), 2.98 (s, 3H, SCH₃), 6.90–8.10 (m, 11H, Ar-H), 13.3 (s, 1H, OH); IR cm⁻¹: 1727 (C=O), 1591–1458 (C=C); Elemental analysis calculated for C₂₁H₁₈O₃N₂S: %C 66.66, %H 4.76, %N7.40, %S 8.46. found: %C 66.96, %H 4.77, %N 7.51, %S 8.58.

3-hydroxy-4-((*p*-tolylidzenyl)methyl)phenyl-4-ethylthio)benzoate (**E-SR₂**): Orange solid; yield% 40; ¹H-NMR (CDCl₃): ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 2.43 (s, 3H, CH₃), 3.00 (q, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3(s, 1H, OH); IR cm⁻¹: 1730 (C=O), 1452–1604 (C=C); Elemental analysis calculated for C₂₂H₂₀O₃N₂S: %C 67.34, %H 5.10, %N 7.14, %S 8.16. found: %C 67.54, %H 5.12, %N 7.18, %S8.21.

3-hydroxy-4-((*p*-tolylidzenyl)methyl)phenyl-4-propylthio)benzoate (**E-SR₃**): Orange solid; yield% 43; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (Hextet, 2H, CH₂), 2.42 (s, 3H, CH₃), 2.98 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3 (s, 1H, OH) (Figure 5); IR cm⁻¹: 1732 (C=O), 1450–1600 C=C); Elemental analysis calculated for C₂₃H₂₂O₃N₂S: %C 67.98, %H 5.41, %N 6.89, %S 7.88. found: %C 68.29, %H 5.51, %N 6.94, %S 7.93.

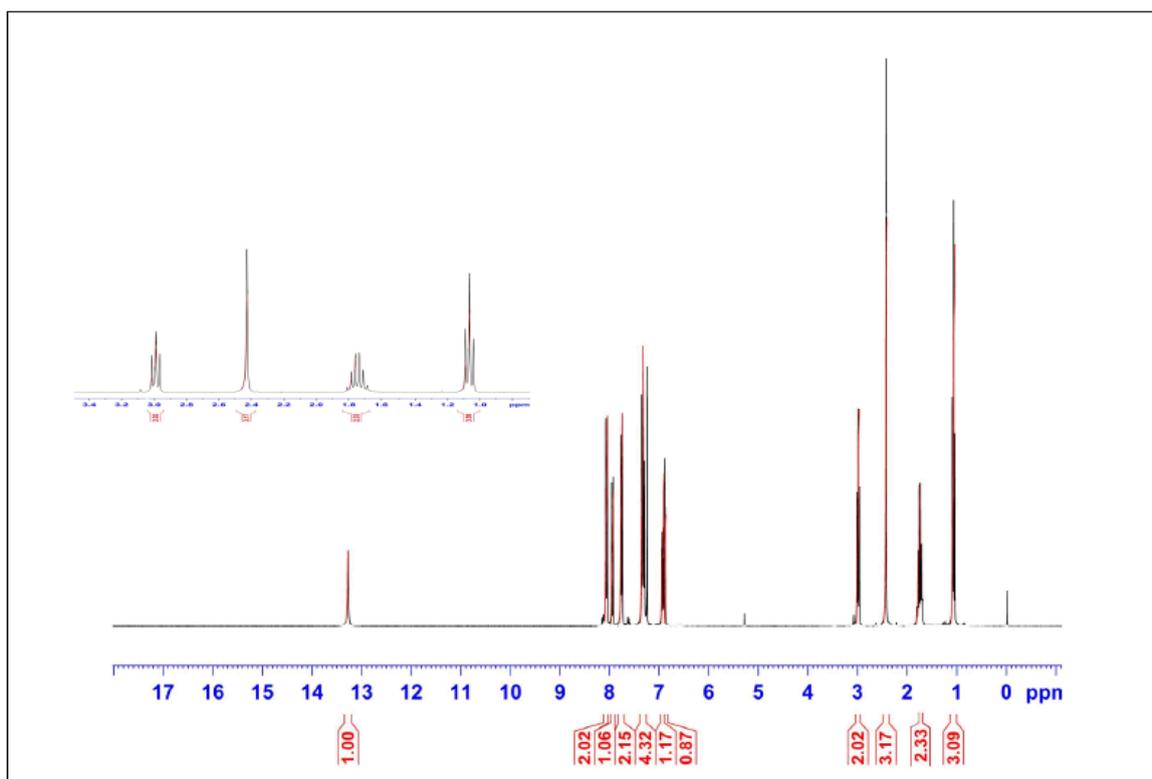
3-hydroxy-4-((*p*-tolylidzenyl)methyl)phenyl-4-butylthio)benzoate (**E-SR₄**): Orange solid; yield%56; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.60 (P, 2H, CH₂), 1.75 (Hextet, 2H, CH₂), 2.42(s, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3(s, 1H, OH), IR cm⁻¹: 1725 (C=O), 1456–1590 (C=C); Elemental analysis calculated for C₂₄H₂₄O₃N₂S: %C 68.57, %H 5.71, %N 6.66, %S 7.61. found: %C 68.75, %H5.79, %N 6.84, %S 7.72.

3-hydroxy-4-((*p*-tolylidzenyl)methyl)phenyl-4-pentylthio)benzoate (**E-SR₅**): Orange solid; yield%58; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (P, 2H,CH₂, 1.60–1.31 (m, 4H, (CH₂)₂, 2.42 (s, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3(s, 1H, OH); IR cm⁻¹: 1721 (C=O), 1450–1596 (C=C); Elemental analysis calculated for C₂₅H₂₆O₃N₂S: %C 69.12, %H 5.99, %N 6.45,%S 7.37 found: %C 69.34, %H 6.07, %N 6.53, %S 7.43.

3-hydroxy-4-((*p*-tolylidzenyl)methyl)phenyl-4-hexylthio)benzoate (**E-SR₆**): Orange solid; yield%60; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (P, 2H, CH₂, 1.29–1.31 (m, 6H, (CH₂)₃, 2.42 (s, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3 (s, 1H, OH); IR cm⁻¹: 1728 (C=O) 1455–1600 (C=C); Elemental analysis calculated for C₂₆H₂₈O₃N₂S: %C 69.64, %H 6.25, %N 6.25, %S 7.14. found:%C69.94, %H 6.27, %N 6.29%, S 7.19.

3-hydroxy-4-((p-tolyldizenyl)methyl)phenyl-4-heptylthio)benzoate (E-SR₇): Orange solid; yield%66; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (P, 2H, CH₂, 1.29–1.31 (m, 8H, (CH₂)₄), 2.42 (S, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3 (S, 1H, OH); IR cm⁻¹: 1726 (C=O), 1451–1595 (C=C); Elemental analysis calculated for C₂₇H₃₀O₃N₂S: %C 70.12, %H 6.49, %N 6.06, %S 6.92. found: %C 70.37, %H6.55, %N6.13, %S 6.97.

Figure 5. ¹H-NMR for E-SR₃ with expansion for aliphatic protons.



3-hydroxy-4-((p-tolyldizenyl)methyl)phenyl-4-octylthio)benzoate (E-SR₈): Orange solid; yield%73; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (P, 4H, CH₂, 1.29–1.31(m, 14H, (CH₂)₅), 2.42 (S, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3 (S,1H,OH); IR cm⁻¹: 1748(C=O), 1451–1599 (C=C); Elemental analysis calculated for C₂₈H₃₂O₃N₂S: %C 70.58, %H 6.72, %N 5.88, %S 6.72. found: %C70.76, %H6.77, %N 5.93 %S6.79.

3-hydroxy-4-((p-tolyldizenyl)methyl)phenyl-4-nonylthio)benzoate (E-SR₉): Orange solid; yield%73; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (P, 4H, CH₂, 1.31–1.42 (m, 12H, (CH₂)₆), 2.42 (S, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3 (S, 1H, OH); IR cm⁻¹: 1728 (C=O), 1453–1601 (C=C); Elemental analysis calculated for C₂₉H₃₄O₃N₂S: %C 71.02, %H 6.93, %N 5.71, %S 6.53. found: %C71.24, %H6.98, %N5.78, %S 6.60.

3-hydroxy-4-((p-tolyldizenyl)methyl)phenyl-4-decylthio)benzoate (E-SR₁₀): Orange solid; yield%76; ¹H-NMR (CDCl₃): 1.07 (t, 3H, CH₃), 1.75 (P, 4H, CH₂, 1.29–1.31 (m, 14H, (CH₂)₇), 2.42 (S, 3H, CH₃), 3.00 (t, 2H, SCH₂), 6.90–8.10 (m, 11H, Ar-H), 13.3 (S, 1H, OH); IR cm⁻¹: 1728 (C=O),1452–1600 (C=C); Elemental analysis calculated for C₃₀H₃₆O₃N₂S: %C 71.42, %H 7.14, %N5.55, %S 6.34. found: %C71.71, %H7.18, %N5.61, %S 6.38.

4. Conclusions

New azo mesogenic compounds with a thioalkyl chain on the terminal of the benzene ring were synthesized. The study indicates that the length of the thioalkyl chain has an effect on the mesomorphic properties, *i.e.*, the temperature range of the nematic phase and melting points decrease with increasing the chain length, however, the large size of the sulfur atom prevents the smectic phase from appearing.

References

1. Johnson, J.F.; Porter, R.S. *Liquid Crystals and Ordered Fluids*; Plenum Press: New York, NY, USA, 1970; p. 477.
2. Smith, G. *Advanced in Liquid Crystals*; Academic Press: New York, NY, USA, 1975; p. 20.
3. Gennes, P. *The Physics of Liquid Crystal*; Clarendon Press: Oxford, UK, 1975; p. 85.
4. Gray, G. *Thermotropic Liquid Crystals*; Wiley: New York, NY, USA, 1987; p. 113.
5. Chandrasekhar, S. *Liquids Crystals*; Cambridge University Press: London, UK, 1977; p. 51.
6. Rene, P.; Jorg, A.S.; Carsten, T. Synthesis and thermotropic liquid crystalline properties of calamitic molecules with laterally attached hydrophilic: Y-shaped three-block molecules which can form smectic and columnar mesophases. *J. Mater. Chem.* **1998**, *8*, 2611–2626.
7. Takeharu, H.; Masahiro, T.; Keiko, I.; Kanji, K.; Akira, M.; Yoshimasa, F. Solid-phases Synthesis of Liquid Crystalline isoxazole library. *Tetrahedron Lett.* **2004**, *45*, 2277–2279.
8. Ha, S.T.; Ony, L.K.; Sivasothy, Y.; Yeap, G.Y.; Lin, H.C.; Lee, S.L.; Boey, P.L.; Bonde, N.L. Mesogenic Schiff base esters with terminal chloro group: Synthesis, thermotropic properties and X-ray diffraction studies. *Int. J. Phys. Sci.* **2010**, *5*, 564–575.
9. Ha, S.T.; Yeap, G.Y.; Boey, P.L. Synthesis and smectogenic A and C* Properties of (S)-(-)-2-Methylbutyl 4'-(4"-n-alkanoxyloxybenzoyloxy)biphenyl-4-carboxylates. *Int. J. Phys. Sci.* **2010**, *5*, 182–191.
10. Chang, C.Y.; Chien, S.Y.; Hsu, C.H.; Gauza, S.; Wu, S.T. Synthesis of laterally substituted α -methylstilbene-tolane liquid crystals. *Liq. Cryst.* **2008**, *35*, 1–9.
11. Jayrang, S.D.; Meera, M. Azomesogens with a heterocyclic moiety. *Bull. Mater. Sci.* **2000**, *23*, 237–238.
12. Prajapati, K.; Pandya, H. Azomesogens with 1,2,4-trisubstituted benzene moiety. *Bull. Mater. Sci.* **2002**, *25*, 355–358.
13. Prajapati, K.; Vora, H. Azomesogens with methoxyethyl tail: Synthesis and characterization. *J. Chem. Sci.* **2005**, *117*, 255–261.
14. Uhood, J.A.; Gassim, T.; Radhy, H. Synthesis and characterization of azo compounds and study the effect of substituents on their liquid crystalline behavior. *Molecules* **2010**, *15*, 5620–5628.
15. Lee, C.H.; Jeong, N.H. Synthesis of novel 3,3-dimethyl-2,2-bipyridyl derivatives having Nematic Liquid-Crystalline and Photoluminescent properties. *J. Ind. Eng. Chem.* **2002**, *8*, 103–107.
16. Chauhan, M.B.; Bhoi, D.K.; Machhar, M.T.; Solanki, D.K.; Dhaval, S. Synthesis, characterization and mesomorphic properties of azoester mesogen: 4-N-alkoxy benzoic acid 4-[3-(benzylidene-amino)-henylazo]-phenyl ester. *Der Pharma Chemica* **2010**, *2*, 30–37.

17. Thaker, B.T.; Patel, P.H.; Vanasadiya, A.D.; Kanojiya, J.B. Substitution effects on the Liquid Crystalline properties of Thermotropic Liquid Crystals Containing Schiff Chalcone Linkages. *Mol. Cryst. Liq. Cryst.* **2009**, *515*, 135–147.
18. Gray, G.W. *Molecular Structure and the Properties of Liquid Crystals*, 2nd ed.; Academic Press: London, UK, 1969; p. 235.
19. Gray, G.W.; Winsor, P.A. *Liquid Crystals and Plastic Crystals*, 1st ed.; Ellis Horwood Press: New York, NY, USA, 1974; p. 103.
20. Ha, S.T.; Yeap, G.Y.; Boey, P.L. Synthesis and Liquid Crystalline Properties of New Schiff Bases *N*-[4-(4-*n*-Alkanyloxybenzoyloxy)benzylidene]-4-cyano-, 4-Hydroxy-, Thio-4-Nitroanilines. *Austr. J. Basic Appl. Sci.* **2009**, *3*, 3417–3422.
21. Singh, A.K.; Kumari, S.; Kumar, K.R.; Sridhar, B.; Rao, T.R. Synthesis and spectral studies of the mesogenic Schiff-base, *N,N*-di-(4'-pentyloxybenzoate)salicylidene-1,8-diamino-3,6-dioxactane and crystal structure of the Zn (II) complexes. *Polyhedron* **2008**, *27*, 181–186.

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