ARTICLE / INVESTIGACIÓN

Synthesis and characterization of azo liquid crystal compounds based on 5H-Thiazolo [3,4-b][1,3,4] thiadiazole unit

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Abstract: A calamitic symmetric liquid crystalline consisting of an azo group containing 5H-Thiazolo[3,4-b][1,3,4]thiadiazole moiety compound[III] was synthesized via sequence reactions starting from reaction terephthaldehyde with mercaptoacetic acid and thiosemicarbazide in the presence of concentrated sulfuric acid to synthesized 5,5'-(1,4-phenylene)bis(5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-amine)[I] then the azo compound [II] synthesized by coupling between diazonium salt of the compound [I] with phenol at (0-4)℃., after that the compound [III] was synthesized by the reaction of the compound [II] with methyl bromide in alkaline media. The compounds are characterized by melting points, FTIR and ^{1}HNMR spectroscopy. The mesomorphic behavior was studied by using polarized optical microscopy POM.

Key words: Azo compounds, liquid crystal, mesomorphic properties.

Introduction

Calamitic liquid crystals (LCs) are widely used in LC displays and optical systems because of the suitability of their anisotropic properties[1-3]. In the case of liquid crystals, the azo group is the most widely employed photochromic unit[4-9]. This is mainly due to its linearity, diversity in preparation[10], speed and stability of isomerization[11]. However, their thermal and optical properties can be adjusted by modifying the molecular geometries of the mesogenic compounds. Several calamitic azo LC derivatives have been investigated and evaluated based on their optical properties[12,13], a few groups have increasingly worked with calamitic azo LC derivatives with different core sizes to determine the location of azo linkages within the rigid portion, lateral groups and terminal flexible-chains length[14-21]. A rigid shape creates azobenzene molecules, essential for exhibiting mesomorphic phenomena[22,23]. Therefore, from these geometrical investigations and part of our study of liquid crystal derivatives containing heterocyclic units[24-29] the purpose of this research was to develop the synthesis of a new azo LC material containing 5H-thiazolo[4,3-b]-1,3,4-thiadiazole unite and methoxy terminal group and the correlation between the geometry of its mesogenic part and its mesomorphic properties.

Materials and methods

Experimental

The materials were taken from Aldrich, Fluka and Merck Co.

Techniques

FT-IR spectra were recorded by SHIMADZU (IR Affinity-1) FT-IR spectrometer in the wave number range 4000-600 cm^{-1}. ^{1}H-NMR spectra were measured by company: Bruker 400 MHz and were reported in ppm (δ); the compounds were dissolved in DMSO- d6 solution with the TMS as the internal standard. The melting point measurement by, Gallen Kamp apparatus. Liquid crystalline properties were investigated by using a (Meiji MT9000) Polarizing Optical Microscope attached to an INSTEC Hot stage.

Synthesis

The route of synthesized new compounds is represented in figure 1.

Synthesis of 5,5'-(1,4-phenylene)bis(5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-amine)[I]

Terephthalaldehyde (1.34 gm, 0.01 mol) and mercaptoacetic acid (1.84 g, 0.02 mol) were mixed for 20-25 min. Then thiosemicarbazide (1.5 gm, 0.02 mol) was added, followed by the addition of concentrated sulfuric acid (15 mL) portion-wise upon cooling. The mixture was kept in the freezer for 24 h. Then treated with crushed ice 40 gm, adding aqueous sodium hydroxide 40% to obtain pH=7-8. The precipitate was filtered[30], dried and recrystallized from ethanol.

Molecular formula: $C_{14}H_{12}N_6S_4$, Yield 60 %, Color yellow, M.P= dec.270 °C. FTIR (v/cm^{-1}): 3456-3194 (asym.,sym NH_2), 3005 (Ar-H), 1643 (C=N), 1589 (C=C). ^{1}H NMR (400MHz, DMSO-d6) δ (ppm): 8.64-6.96 (4H, Ar-H), 5.31 (s,4H,2NH_2), 3.42(2H (2S-CH-N) in cyclic),3.27 (2H (2S-CH=C) in cyclic).

Synthesis of 4,4'- (5,5'- (1,4-phenylene) bis (5H-thiazolo [4,3-b][1,3,4] thiadiazole-5,2-diyl))bis (diazene-2,1-diyl) diphenol[II]

Compound [I] (0.32 g, 0.0017 mol) was dissolved by heating and stirring in 16 mL of 85% phosphoric acid, cooled to 0°C in an ice bath. 4 mL concentrated nitric acid, and

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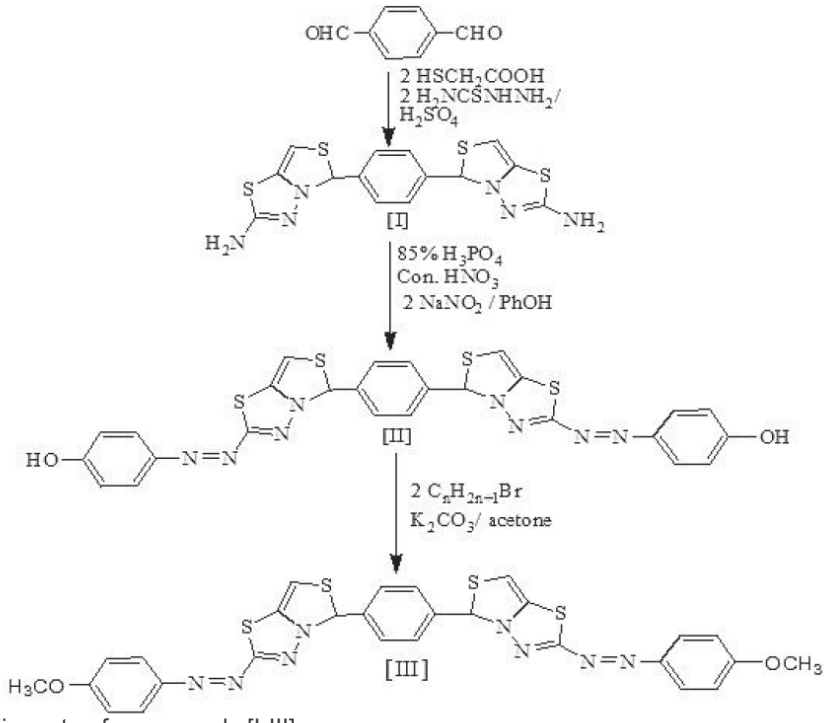

Figure 1. The synthetic route of compounds [I-III].

a solution of (0.23 g, 0.0034 mol) sodium nitrite in 4 mL water was added. React mixture was stirred at 5°C for 10 minutes, then a solution of (0.32 g, 0.0034 mol) phenol in 1 mL water was added to it; the brown product was formed, filtered, washed with water, then dissolved in 60 mL 10% NaOH, the solution was filtered, the crude product was precipitated during neutralization with 10% HCl, then filtered and washed with water several times, recrystallized from ethanol to give brown solid.

Molecular formula: $C_{26}H_{18}N_8O_2S_4$, Yield 80%, Color brown ,M.P>270°C.

FTIR (v/cm-1):3556(OH), 3050 (C-H arom), 1666 (C=N), 1600 (C=C), 1543(N=N)

1,4-bis(2-((4-methoxyphenyl)diazenyl)-5H-thiazolo [4,3-b][1,3,4]thiadiazol-5-yl)benzene [III]

A mixture of compound [II] (1.2 g, 0.0015 mol) and anhydrous potassium carbonate (0.80 g, 0.012 mol) dissolved in acetone 20 mL, then methyl bromide (0.004 mol) was added, the mixture was refluxed overnight. Afterward, the mixture was poured onto ice water; the precipitate was filtered and then washed with water.

Molecular formula: $C_{28}H_{22}N_8O_2S_4$, Yield 90%, Color deep yellow, M. P >300C°

FTIR (v/cm^{-1}):3005 (C-H arom), 2958-2835(C-H aliph), 1651(C=N), 1597(C=C arom), 1573(N=N), ^{1}H NMR (400MHz, DMSO-d6) δ (ppm): (7.75-6.44) (12H, Ar-H),(3.87-3.73) (4H (2S-CH-N) and (2S-CH=C) in cyclic), 2.30 (6H,2OCH$_3$).

Results

The new synthesized compounds characterization by FTIR and ^{1}HNMR spectroscopy gave analysis satisfactory for the proposed structures. Compound [I] was synthesized by treating terephthalaldehyde compound with mercaptoacetic acid and thiosemicarbazide in H_2SO_4 at reflux. This compound characterization by FTIR and ^{1}HNMR spectroscopy. FTIR spectroscopy for compound [I] showed absorption bands at (3456-3194) cm^{-1} which assigned to asymmetry and symmetry of NH_2 and NH groups (Tautomerism NH_2 with C=N in cyclic) also C=N groups were appeared at 1643 cm^{-1}. Also showed absorption bands at 3005 cm^{-1} and 1589 cm^{-1} for C-H and C=C aromatic groups, respectively.

The ^{1}HNMR spectrum (in DMSO-d6 as a solvent) of compound [I], showed: a singlet signal at δ11.49 ppm for protons of NH group (tautomerization NH_2 with C=N in cyclic); many signals in the region δ (8.64-6.96) ppm for four aromatic protons of benzene rings, a single signal at δ 5.31 ppm due to four protons of two (NH_2) groups, a single signal at δ3.42 ppm for two protons of S-CH-N groups also a singlet signal at δ3.27 ppm for two protons of S-CH=C groups.

The azo compound[II] synthesized by coupling between diazonium salt of the 5,5'-(1,4-phenylene)bis(5H-thiazolo[4,3-b][1,3,4]thiadiazole-2amine)[I] with phenol at (0-4)°C. The FTIR spectrum of compound [II] showed disappearance absorption stretching bands of NH_2 groups for starting material compound[I] and appearance stretching bands of hydroxyl 3556 cm^{-1}. Also showed bands at (3050), 1666 cm^{-1}, 1600cm^{-1} and 1543 cm^{-1} for C-H aromatic, C=N, C=C and N=N groups, respectively.

The compound [III] was formed from the reaction of the compound [II] with two moles from methyl bromide with K_2CO_3 in acetone. The FTIR spectrum for compounds [III] showed the disappearance of stretching bands for hydroxy groups for starting material and showed absorption stretching bands of C-H aliphatic of methoxy groups in the region 2958-2835cm^{-1}.

Discussion

Liquid crystalline properties

The phase transition temperatures and mesophase

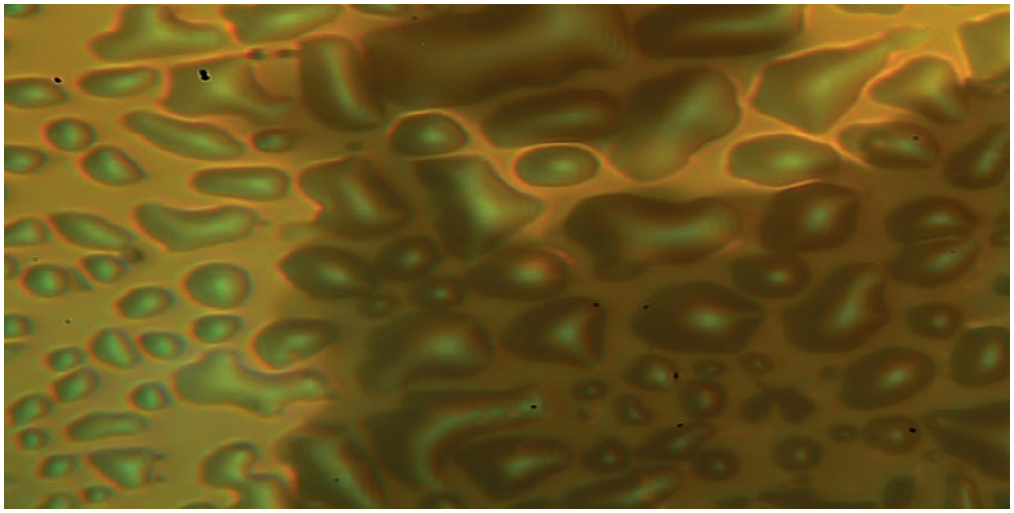

Figure 2. Cross-polarizing Optical textures of nematic phase obtained on heating at 190 C°(Magnification 200×) for compound [III].

type (texture identity) of the compound was investigated by using POM. The mesophases exhibited by compound of series [III] were identified according to their optical textures, which were observed by POM, using the classification systems reported by Sackmann and Demus and Richter[31, 32] and Gray and Goodby[33].The compound [III] showed droplets nematic phase as in figure 1

Conclusions

This work investigated the design and synthesis of a new azo liquid crystalline compound including 5H-thiazolo [3,4-b],[1,3,4] thiadiazole linked with a methoxy group as the terminal chain length, which was then characterized. The melting points, FTIR, and 1HNMR spectroscopy of the compounds are used to describe them. POM (polarized optical microscopy) was used to investigate the mesomorphic behavior of the material.

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