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Synthesis and Liquid Crystalline Behavior of New Amides and Esters Containing ١,٣- Thiazole Ring

Nisreen H. Karam*, Jumbad H. Tomma*, Ammar H. AL-Dujaili* and Nasreen R. Jber**
*Department of Chemistry, College of Education Ibn Al- Haitham, University of Baghdad, Baghdad -Iraq.
**Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

Abstract

Synthesis and study liquid crystalline properties of new compounds with terminal groups of amides ([III]$_{a-c}$,[IV]$_{a-c}$ and [VI]$_n$), alkoxy series[V]$_n$ or ester with azo linkage ([IX]$_{a-c}$ and[X]$_{a-c}$) containing thaizole ring. These series were synthesized by many steps starting from ٤-hydroxyacetophenone or ٤-aminoacetophenone.

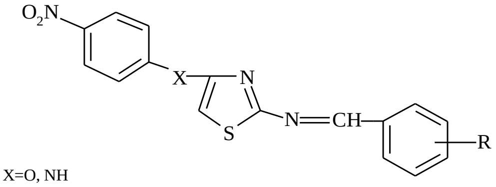
The synthesized compounds were characterized using melting points, FTIR, C.H.N.S analysis and for some of them ^{١}H NMR spectroscopy. The liquid crystalline properties were studied by hot stage polarizing microscopy and differential scanning calorimetry DSC. All compounds of series [III]$_{a-c}$,[IV]$_{a-c}$ and compounds [V]$_n$ showed enantiotropic liquid crystal. While the series [VI]$_n$ showed nematic mesomorphism except [VI]$_{٨}$ did not show any mesomorphic behavior, also the compounds [IX]$_{a, b}$ and [X]$_{a, b}$ showed nematic liquid crystalline, but the compounds[IX]$_c$ and [X]$_c$ did not show any liquid crystalline properties.

Keywords**:** Thiazole, amides, azo compounds, liquid crystal, heterocyclic.

Introduction

Thiazole is very important structural feature in liquid crystals properties[١]. Some functional groups have proven to be very useful to promote mesomorphic properties. For example, the amide and ester groups are some of the most commonly used, as below.

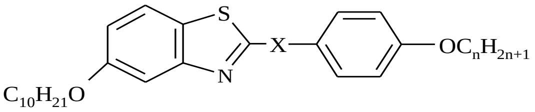
Kuvatov and coworkers, have synthesized and study liquid crystal properties for series containing a thiazole ring [١] with different terminal substituents (R)[٢].



X=O, NH
R=2-F, 3-Br, 4-Cl, 2-NO$_2$, 4-NO$_2$, 4-NMe$_2$, 2,4-(OMe)$_2$

[1]

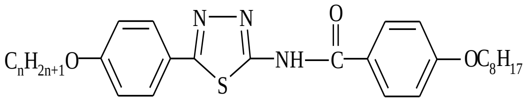
Belmar and coworker, have synthesized a series of benzothiazole derivatives [٢] of liquid crystals within two different linkage groups (amide and azo) and compared with series of imines[٣]. The compounds with imine and azo linkages showed typical nematic and smectic C mesophases, while the compounds with amide linkage showed a poorer mesomorphism and mainly present a smectic C mesophase.



X= NHCO, N═N , N=CH
n= 3-10

[2]

In addition, synthesized and studied liquid crystalline properties of a new series of amides with١,٣,٤-thiadiazole ring [٣], The compounds of series [٣] display nematic (N) and smectic C (SC) mesomorphism in the whole range of n studied[٤].



n=5-10

[3]

Also, synthesized liquid crystalline amide compounds[٥-٧]. Many workers synthesized and study a new series of asymmetric bent-core compounds using azo linkages with equal as well as unequal terminal alkyl chains[٨].

In this study we present the synthesis and mesomorphic behavior of new compounds of thiazole ring with different terminal groups (amide, alkoxy or ester).

Experimental

Chemicals

All chemicals were supplied by fluka, merek and Aldrich chemicals Co. with ٩٠٪ purity at least.

Techniques

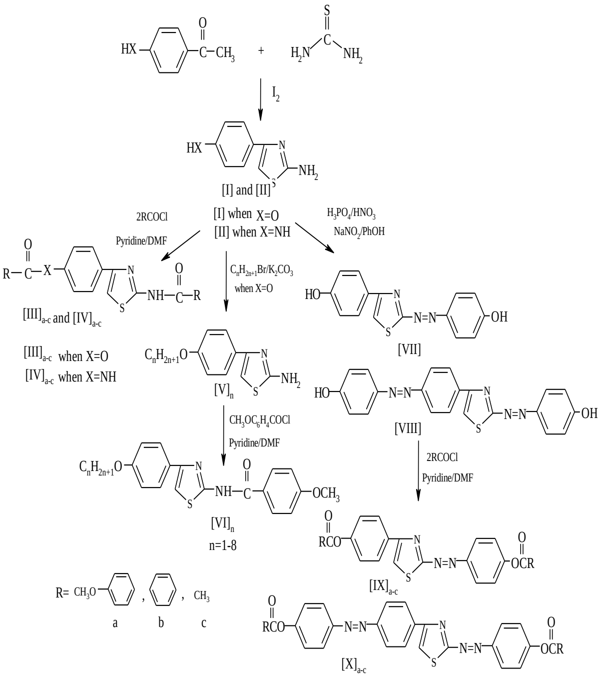
FTIR spectra were recorded on a Shimadzo (Ir prestige-٢١) using potassium bromide discs.^{١}H NMR spectra were carried out on Bruker, ultra-shield ٣٠٠ MHz Switzerland and are reported in ppm(δ), DMSO and CDCl$_{٣}$ were used as solvents with TMS as an internal standard. Elemental micro-analyses of some compounds were performed on a (C.H.N.S) : Euro vector, EA ٣٠٠٠A origin: Italy. Amman, Jordan.

Uncorrected melting points were determined using Hot-Stage, Gallen Kamp melting point apparatus.

The transition temperatures and textures of the mesophases were determined using polarized optical microscope model MT٩٩٣٠ with hot-stage type INSTEC MK١٠٠٠ and DSC measurements were conducted with DSC-٦٠ SHIMADZU and TA-٦٠ WS instruments.

Synthesis

The following scheme١ shows the whole synthesis in this study:



Scheme (١) reaction steps for the synthesis.

Synthesis of ٢-Amino ٤-(٤`-hydroxy or aminophenyl)-١,٣-thiazole[I] and [II]

In a ٢٥٠ mL round bottom flask ٧,٦١g(٠,٠٣mol) iodine was added, thioura (٤,٥٦g,٠,٠٠٦mol) and ٤-hydroxyacetophenone or ٤-aminocetophenone (٠,٠٠٣ mol) were added and the mixture was heated for ٨ hrs. on water bath. Cooling, the resulting solid was washed with diethyl ether and a solution of sodium thiosulfate, the precipitate was filtered[٩] and recrystallized from ethanol.

compound[I] ;yield ٨٩٪, m.p= ١٤٨-١٥٠ °C
compound[II]; yield ٨٣٪,m.p= ١١٠-١١١ °C.

Synthesis of ٢-N-(aryl or methyl amide)-٤-[(٤`aryl or methyl carboxylate or amide) phenyl]-١,٣-thiazole[III]$_{a-c}$ and[IV]$_{a-c}$

The compound [I] or [II] (٠,٠٠١ mol) was dissolved in (١ m L pyridine and ٢ mL DMF) in ice bath and acid chloride (٠,٠٠٢ mol) was added, the mixture stirred for ٣ hrs at room temperature, afterward added ١٠٪ HCl, the precipitate was filtered and washed with water, dried and recrystallized from ethanol.

٢-N-(٤`-methoxybenzamide)-٤-[٤``-(٤```methoxybenzoate)phenyl]-١,٣-thiazole[III]$_{a}$yield٨٥%;FTIR:٣٤٠٨(N-H),٢٩٦٠-٢٨٤٣(C-H)aliphatic,١٧٣٢(C=O) ester,١٦٨٥(C=O) amide,١٦٠٦(C=C) aromatic, ١١٦١(C-O) ester.

٢-N-benzamide-٤-(٤`-benzoate)phenyl-١,٣-thiazole [III]$_{b}$ yield٧٩٪;FTIR:٣٣٩٦(N-H),١٧٤٠(C=O)ester,١٦٧٥(C=O)amide,١٥٩٠(C=C) aromatic, ١١٧٢(C-O) ester .

٢-N-acetamide-٤-(٤`-acetate)phenyl-١,٣-thiazole [III]$_{c}$yield٨٠٪;FTIR:٣٣٤٠(N-H),٢٩٢٧-٢٨٩٥(C-H)aliphatic,١٧٥١(C=O)ester,١٦٨٩(C=O) amide,١٥٩٨(C=C) aromatic, ١١٦٦(C-O) ester.

٢-N-(٤`-methoxybenzamide)-٤-[٤``-(٤```methoxybenzamide)phenyl]-١,٣-thiazole[IV]$_{a}$yield٨٠٪;FTIR:٣٤١٤(N-H),٢٩٧٢-٢٨٤٥(C-H)aliphatic,١٦٨٥,١٦٦٥(C=O) amide,١٦٠٦(C=C) aromatic.

٢-N-benzamide-٤-(٤`-benzamide)phenyl-١,٣-thiazole[IV]$_{b}$

yield٧٩٪;FTIR:٣٣٤٢,١٦٧٥,١٦٥٣(C=O) amide,١٦٠٠(C=C) aromatic

٢-N-acetamide-٤-(٤`-acetamide)phenyl-١,٣-thiazole[IV]$_{c}$yield٧٥٪;FTIR:٣٤١٥(N-H),٢٩٣٥-٢٨٥٠(C-H)aliphatic,١٦٨٠,١٦٥٣(C=O) amide,١٥٩٧(C=C) aromatic.

Synthesis of ٢-Amino ٤-(٤`-n-alkoxyphenyl)-١,٣-thiazole[V]$_{n}$

The compound [I] (٠,٢٨g, ٠,٠٠١٥mol) and anhydrous potassium carbonate (٠,٨٠g, ٠,٠١٢ mol) were dissolved in acetone ٢٠ mL, next n-alkyl bromide (٠,٠٠٤ mol) was added, the mixture was refluxed overnight and poured into ice water. The precipitate filtered and washed with water[١٠], the solid residue was dried and recrystallized from ethanol.

٢-amino٤-(٤`-methoxyphenyl)-١,٣-thiazole[V]$_{١}$

Yield ٦٠٪; FTIR: ٣٤٤١,٣٢٧٣, ٣١١٨($NH_{٢}$), (N-H), ٢٩٩٧-٢٨٣٧(C-H) aliphatic, ١٦٢٥(C=N) endocyclic, ١٦٠٦ (C=C) aromatic, ١٢٩٢(C-O) ether.

٢-amino٤-(٤`-ethoxyphenyl)-١,٣-thiazole[V]$_{٢}$

Yield ٦٥٪; FTIR: ٣٤٤٦, ٣٢٧٥, ٣١١٦($NH_{٢}$), (N-H), ٢٩٨٠-٢٨٧٧ (C- H) aliphatic, ١٦٢٩ (C=N) endocyclic, ١٦٠٦(C=C) aromatic, ١٢٨٨ (C-O) ether.

٢-amino٤-(٤`-n-propoxyphenyl)-١,٣-thiazole [V]$_{٣}$

Yield ٨٣٪; FTIR: ٣٤٥٢, ٣٢٨٨, ٣١٧٠($NH_{٢}$), (N-H), ٢٩٧٠-٢٨٧٢(C- H) aliphatic, ١٦٢٥(C=N) endocyclic, ١٦٠٦ (C=C) aromatic, ١٢٨٦(C-O) ether.

٢-amino ٤- (٤`-n-butoxyphenyl)- ١,٣-thiazole [V]$_{٤}$

yield ٧٥٪; FTIR: ٣٤٢١, ٣٢٩٢, ٣١٦٧($NH_{٢}$), (N-H), ٢٩٥٤-٢٨٧٠(C- H) aliphatic, ١٦٣٣(C=N) endocyclic, ١٦٠٨(C=C) aromatic, ١٢٨٦(C-O) ether.

٢-amino ٤-(٤`-n-pentoxyphenyl)- ١,٣-thiazole [V]$_{٥}$

Yield ٧٤٪; FTIR: ٣٣٨٣, ٣٣١١, ٣١٢٤($NH_{٢}$), (N-H), ٢٩٥٤-٢٨٦٠ (C- H) aliphatic, ١٦٣٩(C=N) endocyclic, ١٦٠٦(C=C) aromatic, ١٢٨٨(C-O) ether.

٢-amino ٤- (٤`-n-hexoxy phenyl)-١,٣-thiazole [V]$_{٦}$

Yield ٦٧٪; FTIR: ٣٤٤٨, ٣٢٩٦, ٣١٥٥($NH_{٢}$), (N-H), ٢٩٢٩-٢٨٥٦(C- H) aliphatic, ١٦٣٣(C=N) endocyclic, ١٦٠٦(C=C)aromatic, ١٢٩٤(C-O) ether.

٢-amino ٤-(٤`-n-heptoxy phenyl)-١,٣-thiazole [V]$_{٧}$

Yield ٨٣٪; FTIR: ٣٣١٧, ٣١٨٠, ٣١٢٤($NH_{٢}$), (N-H), ٢٩٥٤-٢٨٥٤(C- H) aliphatic, ١٦٤١(C=N) endocyclic, ١٦٠٦(C=C) aromatic, ١٢٨٨(C-O) ether.

٢-amino ٤-(٤`-n-octoxy phenyl)-١,٣-thiazole [V]$_{٨}$

Yield ٧٨٪; FTIR: ٣٤١٢, ٣٣٠٠, ٣١٢٤($NH_{٢}$), (N-H), ٢٩٥٣-٢٨٥٤(C- H) aliphatic, ١٦٣١(C=N) endocyclic, ١٦٠٦(C=C) aromatic, ١٢٨٦(C-O) ether.

Synthesis of ٢-N-(٤`-Methoxybenzamide)-٤-(٤``n-alkoxy phenyl)-١,٣- thiazole [VI]$_{n}$

These compounds were synthesized in a similar way for synthesized compound [III] $_{a-c}$, except using compounds [V]$_{n}$ instead of compound [I] and used ٠,٠٠١ mol instead of ٠,٠٠٢ mol from anisoyl chloride. the product was filtered and recrystallized from ethanol to give new product.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-methoxyphenyl)-١,٣-thiazole[VI]$_{١}$

yield ٧٠٪; FTIR:٣٤١٤(N-H), ٣٠٦٠(C-H) aromatic, ٢٩٨٠-٢٨٤٦(C-H) aliphatic, ١٦٨٨ (C=O) amide, ١٦٢٥ (C=N) endocyclic, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-ethoxyphenyl)-١,٣-thiazole[VI]$_{٢}$

Yield ٦٨٪, FTIR: ٣٤٤٦(N-H), ٣٠٦١(C-H) aromatic, ٢٩٦٠-٢٨٤٥ (C-H) aliphatic, ١٦٨٠ (C=O) amide, ١٦٢٨ endocyclic, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-n-propoxyphenyl)-١,٣-thiazole [VI]$_{٣}$

Yield ٨٥٪; FTIR: ٣٢٩٨(N-H), ٣٠٦٥(C-H) aromatic, ٢٩٨٥-٢٨٤٦ (C-H) aliphatic, ١٦٨٧ (C=O) amide, ١٦٢٥ endocyclic, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-n-butoxyphenyl)-١,٣-thiazole [VI]$_{٤}$

Yield ٧٨٪; FTIR: ٣٤١٥ (N-H), ٣٠٦٤ (C-H) aromatic, ٢٩٥٨-٢٨٤٥ (C-H) aliphatic, ١٦٩٧ (C=O) amide, ١٦٣٧ endocyclic, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-n-pentoxyphenyl)-١,٣-thiazole [VI]$_{٥}$

Yield ٨٠٪; FTIR: ٣٤١٤ (N-H), ٣٠٦٧ (C-H) aromatic, ٢٩٦٠-٢٨٤٦ (C-H) aliphatic, ١٦٦٠ (C=O) amide, ١٦٣٥, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-n-hexoxyphenyl)-١,٣-thiazole [VI]$_{٦}$

Yield ٧٩٪; FTIR: ٣٣٠٠ (N-H), ٣٠٦٥ (C-H) aromatic, ٢٩٥٥-٢٨٤٧ (C-H) aliphatic, ١٦٦٥ (C=O) amide, ١٦٣٠ endocyclic, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-n-heptoxyphenyl)-١,٣-thiazole [VI]$_{٧}$

Yield ٧٧٪; FTIR: ٣٣٨٣ (N-H), ٣٠٦١(C-H) aromatic, ٢٩٥٨-٢٨٤٦ (C-H) aliphatic, ١٦٦٢ (C=O) amide, ١٦٣٢ endocyclic, ١٦٠٨ (C=C) aromatic.

٢-N-(٤`-methoxybenzamide)-٤-(٤``-n-octoxyphenyl)-١,٣-thiazole [VI]$_{٨}$

Yield ٨٣٪; FTIR: ٣٤١٩ (N-H), ٣٠٦١ (C-H) aromatic, ٢٩٦٠-٢٨٥٤ (C-H) aliphatic, ١٦٩٣ (C=O) amide, ١٦٤٣ (C=N) endocyclic, ١٦٠٨ (C=C) aromatic.

Synthesis of ٢-(٤`-Hydroxyphenyl azo)-٤-(٤``-hydroxy phenyl)-١,٣-thiazole [VII] and ٢-(٤`-Hydroxyphenyl azo)-٤-[٤``(٤```-hydroxy phenyl azo) phenyl]-١,٣-thiazole [VIII]

The azo compounds [VII] and [VIII] were synthesized according to literature[١١].

Compound[VII]; yield ٧٥٪, m.p = ١٢٨-١٣٠°C.

Compound[VIII]; yield ٧٠٪, m.p > ٢٩٥°C.

Synthesis of ٢-(٤`-aryl or methyl carboxylate phenyl azo)-٤-(٤``-aryl or methyl carboxylate phenyl)-١,٣-thiazole [IX]$_{a-c}$ and ٢-(٤`-Aryl or methyl carboxylate phenyl azo)-٤-[٤``(٤```- aryl or methyl carboxylate phenyl azo) phenyl]-١,٣-thiazole[X]$_{a-c}$

These compounds were synthesized in a similar way for synthesized compound [III]$_{a-c}$, except using the compounds [VII] and [VIII], respectively instead of compound [I], the product was filtered and recrystallized from ethanol to give new product.

٢-[٤`-(٤``-methoxy benzoate) phenyl azo]-٤-[٤```-(٤````- methoxy benzoate) phenyl]-١,٣-thiazole [IX]$_a$

Yield ٧٩٪; FTIR: ٢٩٩٦-٢٨٤٥(C- H) aliphatic, ١٧٣٥, ١٦٨٥ (C=O) ester, ١٦٠٤ (C=C) aromatic, ١٥٤٥ (N=N), ١٢٢٢(C-O) ester.

٢-(٤`-benzoatephenylazo)-٤-(٤``-benzoatephenyl)-١,٣-thiazole [IX]$_b$

Yield ٧٠٪; FTIR: ١٧٤٩, ١٧٢٤ (C=O) ester, ١٥٩٨ (C=C) aromatic, ١٥٣٠(N=N), ١٢١٣(C-O) ester.

٢-(٤`-acetatephenylazo)-٤-(٤``-acetatephenyl)-١,٣-thiazole [IX]$_c$

Yield ٧٥٪; FTIR: ٢٩٢٦-٢٨٧٠ (C-H) aliphatic, ١٧٢٦, ١٦٧٥ (C=O) ester, ١٥٨٠ (C=C) aromatic, ١٥٣٥(N=N), ١١٨٤(C-O) ester.

٢-[٤`-(٤`` methoxy benzoate)phenyl azo]-٤-[٤``` (٤````- methoxy benzoate phenyl azo)phenyl]-١,٣-thiazole[X]$_a$

Yield ٧٧٪; FTIR: ٢٩٣٧-٢٨٤١ (C-H) aliphatic, ١٧٣٩, ١٧١٤ (C=O) ester, ١٦٠٤ (C=C) aromatic, ١٥٣٣ (N=N), ١٢٢٢(C-O) ester.

٢-(٤`-benzoatephenylazo)-٤-[٤``(٤```-benzoatephenylzo) phenyl]-١,٣-thiazole[X]$_b$

Yield ٨٣٪; FTIR: ١٧٤٣, ١٧٠١ (C=O) ester, ١٥٩٨ (C=C) aromatic, ١٥٢٩ (N=N), ١٢٠٩ (C-O) ester.

٢-(٤`- acetatephenyl azo)-٤-[٤``(٤```- acetate phenyl azo) phenyl]-١,٣-thiazole[X]$_c$

Yield ٦٨٪; FTIR: ٢٩٤٣-٢٨٨١ (C-H) aliphatic, ١٧٥١, ١٧٢٠ (C=O) ester, ١٦٠٤ (C=C) aromatic, ١٥٣٣(N=N), ١٢١٩(C-O) ester.

Results and Discussion

The characteristic FTIR spectra, showed the disappearance of absorption stretching bands of carbonyl group C=O and C=S of starting materials with the appearance of a stretching bands in region (٣٤٥٠-٣١٩٩) cm$^{-١}$ and (٣٣٠٤- ٣١٨٢) cm$^{-١}$ respectively due to NH,NH$_{٢}$ groups and appearance a new stretching band at ١٦٢٢ cm$^{-١}$ and ١٦٢٤ cm$^{-١}$

due to C=N for thiazole ring moiety, respectively.

The ^{١}H NMR spectrum of compound[I] showed the following signals: a singlat signal at δ ٩,٥٣ ppm for one proton could be attributed of OH group, two doublet pair in the region δ (٦,٧٥-٧,٨٢) ppm due to four aromatic protons, a broad signal at δ ٧. ٥٧ ppm for two protons of $NH_{٢}$ group. The signal at δ٦,٧٨ ppm for one proton of thiazole ring[١٢].

The FTIR spectra of compounds [III]$_{a-c}$ (ester and amide) showed a significant bands in the region (١٧٣٢- ١٧٥١) $cm^{-١}$ and (١٦٨٥-١٦٨٩) $cm^{-١}$ which could be attributed to stretching vibration band of the carbonyl of ester and amide group, respectively showed disappearance of stretching absorption bands due to O-H and $NH_{٢}$ of compound [I]. While The FTIR spectra of amides [IV]$_{a-c}$ showed a significant band in the region (١٦٨٥-١٦٥٣)$cm^{-١}$ due to carbonyl of amide group, also showed the disappearance of stretching absorption band due to $NH_{٢}$ group of compound [II].

The ^{١}H NMR spectrum of compound [III]$_{a}$ showed: a singlet signal at δ١٢,٤٠ ppm for proton of NH group, two douplet of douplets in the region δ(٧,١٣-٨,٠٨) ppm could be attributed to twelve aromatic protons of three benzene rings, a weak signal at δ(٧,٣٠) ppm for one proton of thiazole ring, two sharp signals at δ(٣,٨٨) ppm and (٣,٨٢) ppm for six protons of two $OCH_{٣}$ groups.

While the ^{١}HNMR spectrum for amide compound [IV]$_{b}$ showed: signal at δ١٠,٤٠ ppm for two protons of two NH groups, multiplet signal in the region δ(٧,٤٧-٨,١٢) ppm could be attributed to twelve aromatic protons of three benzene rings and signal at δ(٧,٠١) ppm for proton of a thiazole ring.

The FTIR spectra showed the disappearance of the stretching band of OH group and appearance of new absorption stretching bands of the aliphatic C-H group in the region (٢٩٩٧-٢٨٥٤) $cm^{-١}$ for alkyl groups.

Elemental analysis result of compound [V]$_{٥}$ is good agreement with the theoretical data Elemental analysis of compound[V]$_{٥}$:

Calc.: C% = ٦٥,١١, H% = ٦,٩٧, N% = ١٠,٨٥, S% = ١٢,٤٠

Found: C% =٦٤,٨٤, H% = ٦,٦٤, N% = ١٠,٥٥, S% = ١٢,٦١

The FTIR spectra showed disappearance bands of NH,$NH_{٢}$ groups of compounds [V]$_{n}$ with appearance of a new stretching band of NH group in range(٣٤١٤-٣٤١٩) $cm^{-١}$, also appearance carbonyl amide (NHC=O) in range(١٦٨٨- ١٦٩٣) $cm^{-١}$.

The ^{١}HNMR spectrum for compound [VI]$_{٥}$ showed: singlet signal at δ٨,٠٥ ppm for one proton of NH group, two douplet in region δ(٦,٩٣-٨,١١) ppm could be attributed for eight aromatic protons,a singlet signal at δ(٦,٨٨) ppm could be attributed to proton of thiazole ring,a triplet signal at δ(٣,٨٧-٣,٨٩) ppm duo to protons of $OCH_{٣}$ and $OCH_{٢}$ termenal groups, a multiplet signal at δ(١,٤٠-١,٨٢)ppm for six proton of three groups of -$CH_{٢}$- and a triplet signal at δ(٠,٩٣-٠,٩٧) ppm due to three protons of $CH_{٣}$ group.

The azo compounds [VII] and [VIII] were synthesized by coupling between diazonium salt of the amino thiazole [I] or [II], respectively with phenol at ٠-٤ °C. The structure of these compounds were studied by melting points, FTIR and C.H.N.S. analysis. The characteristic FTIR absorption bands showed the disappearance of two absorption bands due to $NH_{٢}$ stretching of compound [I] and [II] together with the appearance of a stretching broad band around ٣٢٩٢ $cm^{-١}$ and (٣٤٠٤-٣٣٤٠)$cm^{-١}$ due to the intermolecular hydrogen bonding of O-H bond, respectively. It also shows a band at ١٥٢١$cm^{-١}$ and ١٥١٦ $cm^{-١}$ due to a stretching band of N=N group, respectively.

Elemental analysis of compound [VII] :

Calc.: C% = ٦٠,٦٠, H% = ٣,٧٠, N% = ١٤,١٤, S% = ١٠,٧٧

Found: C% = ٦٠,٢٢, H% = ٣,٩٠, N% = ١٤,٢٢, S% = ١٠,٦٦

These results are good agreement with proposed structure.

The compounds [IX]$_{a-c}$ and [X] $_{a-c}$ were synthesized by reaction of one mole of compounds [VII] or [VIII] with two moles of different acid chloride, respectively in presence of dry pyridine as acceptor**.** The structures of these compounds were studied by melting points, FTIR and ^{١}HNMR spectroscopy.

The FTIR spectra showed a significant bands in the region (١٧٣٥-١٦٧٥) $cm^{-١}$ and (١٧٣٩-١٧٢٠) $cm^{-١}$ which could be attributed to stretching vibration of the carbonyl of ester groups, respectively. They also showed the disappearance of absorption band due to υ O-H of compounds [VII] and [VIII].

The ^{١}HNMR spectrum for compound [X]$_a$ showed: two doublet in region δ(٧,٠٨-٨,٤٥) ppm could be attributed for aromatic protons of benzene rings and the proton of thiazole ring (which is interference with the aromatic protons of benzene), singlet signal at δ ٤,٠٢ ppm for six protons of two $OCH_٣$ groups.

Mesomorphic properties

The transition temperatures of compounds [III]$_{a-c}$ and [IV]$_{a-c}$ were summarized in Table (١). When compared between two above series, found that compounds[III]$_a$ and[III]$_b$ showed both semactic and nematic phases, while the compound [III]$_c$ and all of compounds [IV]$_{a-c}$ showed only nematic phase, this explain that compounds[III]$_a$ and [III]$_b$ favored a layer smectic order because was fully compatible with a molecular arrangement resulting from the intermolecular H-bonding which develops in the tilt direction and thus stabilizes the tilt of the smectic phase[٣] (as shown in Fig.(١)) in addition these compounds containing three phenyl rings for this reasons, displayed a tilte semactic C mesophase in addition nematic phase.

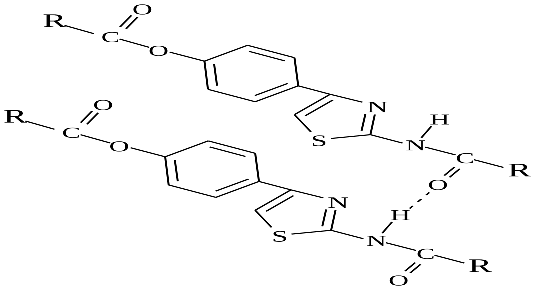
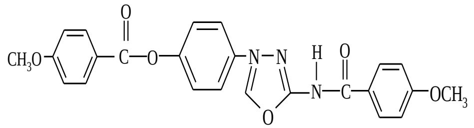


Fig.(١) Hydrogen bonding formation for compounds [III]$_{a,b}$.

But the compound [III]$_c$ containing one phenyl ring and two methyl groups (shorter chain) these decrease in lateral attraction forces and not appears semactic phase. While compounds [IV]$_{a-c}$ did not have ester group and low lateral forces(ratio(t/l) is high) for this reason, the compounds[IV]$_{a-c}$ showed a nematogenic behaviors.

When compared compound [III]$_a$ in this work with compound [٤] in another study[١٣], found the compound [٤] with oxadiazole ring did not show any liquid crystal mesophase, but compound [III]$_a$ with thaizole ring in this study showed Sc and nematic phase.



[4]

While the series [V]$_n$ with n=١-٥ showed only nematic phases but when n=٦-٨ displayed nematic phases and smectic C, as shown in Fig.(٢) for DSC thermogram of compound [V]$_٦$ and Fig.(٣) for smectic C(SmC) texture of compound [V]$_٧$. This behavior can be described to the chain length of alkoxy end group that interferes with liquid crystalline ordering, this could be explain in term of terminal/lateral (t/l) interaction forces ratio. When this ratio is high, compounds tend to give less ordered mesophases (nematic mesophase), While this ratio is low, the compounds tend to give high order mesohpases (smectic phases), the transition temperatures of series [V]$_n$ are given in Table (٢). All compounds of series [VI]$_n$ showed nematic phase, while the compound [VI]$_٨$ failed in the formation of liquid crystalline phase, the transition temperature are given in Table (٣). A plot of transition temperatures against the number (n) of carbon atoms in the lateral alkoxy chain are shown in Fig.(٤). The effects of the terminal chain length on the transition temperatures and phases behavior observed in this series are in accordance with those observed for conventional low molar mass mesogens.

All compounds [IX]$_{a,b}$ and [X]$_{a,b}$ showed only nematic texture, as shown in Figure ٥ for compound [IX]$_b$ but the compounds [IX]$_c$ and [X]$_c$ failed in the formation of liquid crystalline phase. In this case we can explain that the end groups polarizability (acetyl groups) are not large enough to give enantiotropic nematic phase, therefore these compounds did not show appear any liquid crystal phases. The transition temperatures are given in Table (٤).

Table (١)
Phase transition of compounds $[III]_{a-c}$ and $[IV]_{a-c}$.

Compound	Phase transition
$[III]_a$	$Cr \xrightleftharpoons{78} Sc \xrightleftharpoons{95} N \xrightleftharpoons{144} I$
$[III]_b$	$Cr \xrightleftharpoons{95} Sc \xrightleftharpoons{120} N \xrightleftharpoons{162} I$
$[III]_c$	$Cr \xrightleftharpoons{87} N \xrightleftharpoons{99} I$
$[IV]_a$	$Cr \xrightleftharpoons{60} N \xrightleftharpoons{91} I$
$[IV]_b$	$Cr \xrightleftharpoons{118} N \xrightleftharpoons{147} I$
$[IV]_c$	$Cr \xrightleftharpoons{65} N \xrightleftharpoons{100} I$

Table (٢)
Phase transition of series $[V]_n$.

Compound	Phase transition
$[V]_{١}$	$Cr \xrightleftharpoons{155} N \xrightleftharpoons{171} I$
$[V]_{٢}$	$Cr \xrightleftharpoons{235} N \xrightleftharpoons{250} I$
$[V]_{٣}$	$Cr \xrightleftharpoons{132} N \xrightleftharpoons{151} I$
$[V]_{٤}$	$Cr \xrightleftharpoons{73} N \xrightleftharpoons{119} I$
$[V]_{٥}$	$Cr \xrightleftharpoons{109} N \xrightleftharpoons{158} I$
$[V]_{٦}$	$Cr \xrightleftharpoons{74} Sc \xrightleftharpoons{101} N \xrightleftharpoons{185} I$
$[V]_{٧}$	$Cr \xrightleftharpoons{54} Sc \xrightleftharpoons{70} N \xrightleftharpoons{102} I$
$[V]_{٨}$	$Cr \xrightleftharpoons{49} Sc \xrightleftharpoons{85} N \xrightleftharpoons{110} I$

Table (٣)
Phase transition of series $[VI]_n$.

Compound	Phase transition
$[VI]_{١}$	$Cr \xrightleftharpoons{85} N \xrightleftharpoons{122} I$
$[VI]_{٢}$	$Cr \xrightleftharpoons{90} N \xrightleftharpoons{120} I$
$[VI]_{٣}$	$Cr \xrightleftharpoons{83} N \xrightleftharpoons{117} I$
$[VI]_{٤}$	$Cr \xrightleftharpoons{85} N \xrightleftharpoons{105} I$
$[VI]_{٥}$	$Cr \xrightleftharpoons{79} N \xrightleftharpoons{102} I$
$[VI]_{٦}$	$Cr \xrightleftharpoons{83} N \xrightleftharpoons{99} I$
$[VI]_{٧}$	$Cr \xrightleftharpoons{76} N \xrightleftharpoons{91} I$
$[VI]_{٨}$	$Cr \xrightleftharpoons{71-72} I$

Table (٤)
Phase transition of compounds $[IX]_{a-c}$ and $[X]_{a-c}$.

Compound	Phase transition
$[IX]_a$	$Cr \xrightleftharpoons{85} N \xrightleftharpoons{117} I$
$[IX]_b$	$Cr \xrightleftharpoons{45} N \xrightleftharpoons{118} I$
$[IX]_c$	$Cr \xrightleftharpoons{144-145} I$
$[X]_a$	$Cr \xrightleftharpoons{47} N \xrightleftharpoons{89} I$
$[X]_b$	$Cr \xrightleftharpoons{129} N \xrightleftharpoons{231} I$
$[X]_c$	$Cr \xrightleftharpoons{> 295} I$

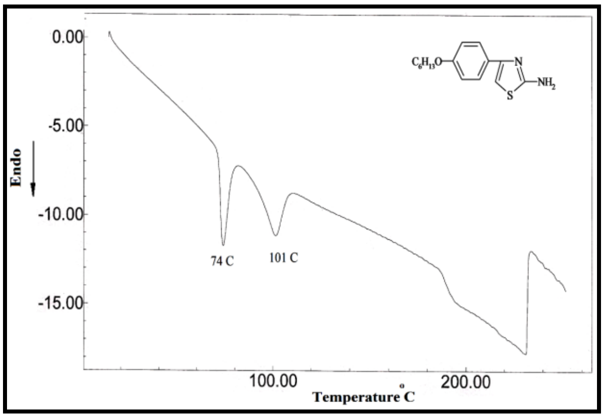


Fig.(٢) DSC Thermogram of compound$[V]_{٦}$.

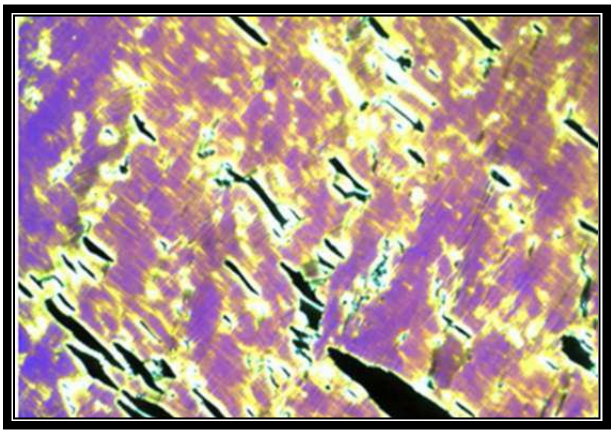


Fig.(٣) Smectic C (SmC) texture of compound $[V]_{٧}$.

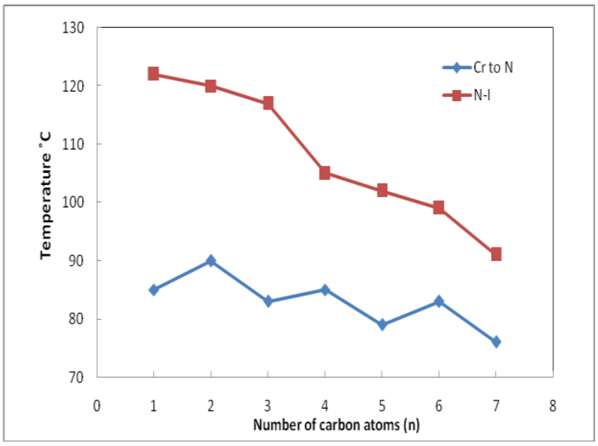


Fig.(٤) Dependence of transition temperatures on the increasing number of carbon atoms (n) in the terminal alkoxy chains for the compounds of series $[VI]_{n}$.

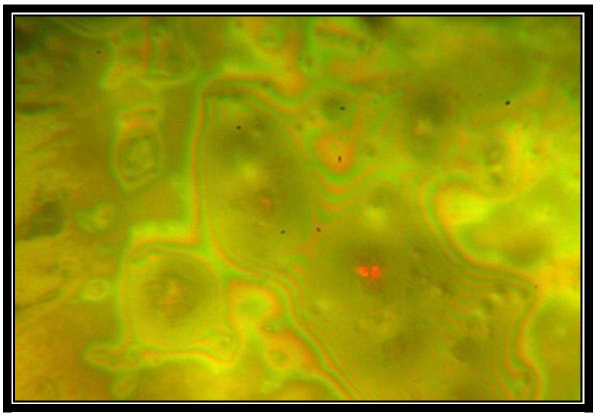


Fig.(٥) Nematic texture of the compound $[IX]_{b}$.

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الخلاصة

تناول هذا البحث تحضير ودراسة الخواص البلورية السائلة لمركبات جديدة تحتوي على مجاميع طرفية أميدية ($[III]_{a-c}$, $[IV]_{a-c}$ و $[VI]_n$), سلسلة الكوكسي $[V]_n$ وأسترية مع رابطة أزو ($[IX]_{a-c}$ و$[X]_{a-c}$) تحتوي على حلقة الثايازول. حضرت هذه السلاسل بعدد من الخطوات تبدأ بـ ٤- هيدروكسي أسيتوفينون أو ٤- أمينو أسيتوفينون .شخصت التراكيب الكيميائية للمركبات المحضرة بواسطة درجات الانصهار FTIR، تحليل C.H.N.S. ولبعض منها طيف ^{1}HNMR، أما الخواص البلورية السائلة فتم دراستها بواسطة مجهر الضوء المستقطب المزود بمنصة تسخين ومسعر المسح التفاضلي DSC. جميع مركبات السلاسل $[III]_{a-c}$,$[IV]_{a-c}$ و$[V]$ أظهرت خواص بلورية سائلة أما مركبات السلسلة $[VI]_n$ فأظهرت طورا نيماتيا ما عدا المركب $[VI]_{٨}$ فأنة لم يظهر أي خواص بلورية سائلة. بالإضافة إلى ذلك المركبات $[IX]_{a,b}$ و $[X]_{a,b}$ أظهرت الطور النيماتي لكن المركبين $[IX]_c$ و $[X]_c$ لم يظهرا أي خواص بلورية سائلة .