Synthesis, Characterization and Study of Mesomorphic Behavior of New Bent and Liner Core Compounds Containing Heterocyclic

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Abstract

We described herein the synthesized and characterized of new bent and liner core compounds containing thiazolidin-4-one ring[XI-XIII] and [XIV-XVI] respectively. These compounds synthesized by sequence reactions starting from reaction resorcinol or hydroquinone with chloracetyl chloride to yield compounds [I] and [II], then the later compounds reactant with 4-hydroxybenzylaldehyde to product dialdehyde compounds [III] and [IV] .The Schiff bases compounds[V-VII] and [VIII-X] synthesized from reaction the compound [III] or [IV] with different aromatic amines, while the bent and liner core mesogens containing thiazolidin-4-one ring [XI-XIII] and [XIV-XVI] synthesized from reaction Schiff bases compounds[V-VII] or [VIII-X] with thioglycolic acid. In addition estrfecation of cinnamic acid with methanol to yield ester compound[XVII]which was converted to their acid hydrazid[XVIII] and the acid hydrazid reacted with glysine in phosphorous oxychloride to yield (5-styryl-1,3,4-oxadiazol-2-yl) methanamine [XIX]. Then reactant the1,3,4-oxadiazol compound[XIX] with dialdehyde compound [III] or [IV] to product new Schiff bases compounds [XX] and [XXI], afterword added thioglycolic acid to give new thiazolidin-4-one derivatives [XXII] and [XXIII], respectively.

The synthesized compounds were characterized by melting points , FTIR ,¹HNMR and mass spectroscopy (of some of them). The liquid crystalline properties were studied by hot stage polarized optical microscopy (POM) and differential scanning calorimetry(DSC). All the Schiff bases compounds [V-X] showed liquid crystals phases while thiazolidin-4-one derivatives[XI-XIII],[XIV-XVI]and [XXIII] didn't show any liquid crystals properties except the compound [XXII] showed enantiotropic nematic phase.

Keywords: liquid crystals; 1,3,4-oxadiazol; resorcinol and hydroquinone.

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Introduction

sensors[3]

In recent years, there has been interest study of liquid crystals resulting in the discovery of many applications in modern technologies, particularly in display devices due to their unusual optical and electrical properties. The banana- shaped liquid crystals are also interested widely, due to its unique electro-optic and photo-induced characteristics [1,2]moreover, these materials are also of significant interest for command surfaces and

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Many workers synthesized bent or liner core liquid crystals compounds containing1,3disubstitutedphenylene or 1,4-disubstitutedphenylene from resorcinol or hydroquinone, respectively, as Ciobanu et. al.[4] synthesized and investigated liquid crystalline behavior of symmetrical non liner liquid crystal containing 1,3- disubstituted benzene ring as a central core also consisting of different linkage groups beside to terminal alkyloxy chain containing 6 to 10 carbon atoms(1).All compounds appeared enantiotropic mesophases (nematic and smectic phases).



Also, Huzum et al.[5]synthesized and studied mesomorphic behavior of two new series of bent core liquid crystalline compounds based on a 1,3-dihydroxybezene core and containing a cholesteryl 6-oxyhexanoate wing. While, Alaasar et al[6]synthesized and investigated bent-core mesogens derived from 4-methylresorcinol with azobenzene wings and terminal group as (OC_nH_{2n+1} ,n=6-22). The short homologues chain exhibit smectic phases and for the longes thomologue only a crystalline phase was observed.

In addition ,Yuvaraj et al.[7]investigated the liquid crystalline and light-induced properties of resorcinol spacer based dimericazobenzene(2),the compound [2]showed nematic and smecticA phases



One the other hand ,synthesized liner core liquid crystals compounds containing 1,4disubstitutedphenylene from hydroquinone as, synthesized three aromatic rigid mesogenicdiols(3) based on hydroquinone and 4-hydroxy benzoic acid as starting materials[8]. The experimental results reveal that hydroquinone based rigid triad mesogenicdiol have higher thermal stability. In the literature, we did not found any studies of the effect of thiazolidin-4-one derivatives on the liquid crystals properties, therefore this paper presents the synthesis, structural characterization and mesomorphic properties of new bent and liner core liquid crystals containing thiazolidin-4-one unit as while as 1,3,4-oxadiazol ring.

(3)

Experimental

Chemicals

All chemicals were supplied by Fluka, Merck and Aldrich chemicals Co. **Techniques**

FT-IR spectra were recorded by 600 FT-IR spectrometer.¹H-NMR spectra were carried company: Bruker ,500 reported out by MHz and were in ppm(δ), DMSO was used as a solvent with TMS as an internal standard, measurements were made at Central lab ,Tehran University. Massspectrum was determined by scan110(1.257min):direct prob-013777.d,at Central lab ,Tehran University.uncorrected melting points were determined by using Hot-Stage, Gallen Kamp melting point apparatus. The transition temperatures and textures of the mesophases were determined using polarized opticalmicroscope model Leica DM2500 Mand DSC measurements were conducted with STAPT-1000LINSIS.

Synthesis

New compounds are synthesized according to scheme1:



Scheme (1)

Preparation of 1,3-phenylene bis(2-chloroacetate) [I]and 1,4-phenylene bis(2-chloroacetate)[II][9,10]

Chloroacetyl chloride (0.002 mol) was slowly added to a stirred solution of resorcinol or hydroquinone (0.11 g ,0.001 mol), pyridine 1 ml and DMF 2 ml at 0 °C. Then, the reaction mixture was stirred for 3 hrs.atroom temperature then, neutralized with saturated sodium bicarbonate solution. The precipitate was filtered and washed with water, dried and the residue was recrystallized from ethanol.

Data compound [I]: reddish color, Yield 70 %, m.p.= $66-68^{\circ}C$

Data compound [II]: white color ,Yield 78 %, m.p.= 122-123^oC

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Synthesis of1,3-phenylene bis(2-(4-formylphenoxy)acetate)[III] and1,4-phenylene bis(2-(4-formylphenoxy)acetate)[IV]

A mixture of compound [I] or [II](0.001mol), 4-hydroxybenzylaldehyde (0.002 mol) and fused sodium acetate (0.246 g, 0.003 mol) in absolute ethanol 5 ml was refluxed for 4 hrs. then cooled and poured into cold water. The precipitate was filtered and recrystallized by ethanol.

Data compound [III]: brown color, Yield 70 %, $m.p = 86-88^{\circ}C$

Data compound [IV]: dark brown color, Yield 68 %, m.p = $58-60^{\circ}$ C

Synthesis of Schiff base compounds [V-VII] and [VIII-X]

A mixture of compound [III] or [IV] (0.001 mol) and different aromatic amines (0.002 mol) were dissolved in 5ml ethanol absolute, refluxed for 3-4 hrs. and cooled to room temperature . the solid product was to give new Schiff bases . The physical properties are listed in Table(1).

Synthesis of thiazolidin-4-onederivatives[XI-XIII] and [XIV-XVI]

A mixture of Schiff bases [V-VII] or [VIII-X] (0.001mol) and thioglycolic acid (0.002 mol) was refluxed in dry benzene (3 ml) for 12 hrs. The solvent was evaporated and residue was neutralized with sodium bicarbonate solution then, the precipitate was filtered. The physical properties are listed in Table (1).

Preparation of Methyl 3-phenyl-2-propenoate[XVII][11]

A mixture of cinnamic acid (36.408 g, 0.246 mol) in absolute methanol (100 ml) and sulfuric acid (3 ml) was refluxed for (6 hrs.) after cooling the mixture was washed with sodium bicarbonate solution, then washed with water several times dried and recrystallized from ethanol. Yield 80 %, m.p= ($36-38^{\circ}$ C)

Preparation of 3-Phenyl-2-propenohydrazide[XVIII]

A mixture of ester compound [XVII] (0.006 mol) and 80% hydrazine hydrate (3 ml) in absolute ethanol (5 ml) was refluxed for (3 hrs). The mixture was cooled at room temperature then solvent was evaporated and solid formed recrystallized from acetone.Yield76 %, m.p115–117.

Synthesis of (5-styryl-1,3,4-oxadiazol-2-yl) methanamine [XIX]

Compound [XVIII](1.62g, 0.01 mol) and glysine(0.75g, 0.01 mol) were refluxed with phosphorous oxychloride (5mL) for 24 hrs. and the reaction mixture was then treated with ice water carefully and made basic by adding concentrated sodium bicarbonate solution. The resulting solid was filtered, dried and recrystallized by ethanol.darkbrown color, Yield 65%,m.p = 166-168 °C

Synthesisof1,3-phenylenebis{2-[4-(((5-styryl-1,3,4-oxadiazol-2-
yl)methylimino)methyl)phenoxy]acetate}[XX]und1,4-phenylenebis{2-[4-(((5-styryl-1,3,4-oxadiazol-2-
yl)methylimino)methyl)phenoxy]acetate}[XX]

These compounds were synthesized by using the same procedure given for synthesis compounds[V-VII] and [VIII-X], except using the compound [XIX] as aromatic amines. Data compound [XX]: browncolor, Yield 77%, m.p = $116-118^{\circ}C$

Data compound [XXI]: brown color, Yield 70%, m.p = $68-70^{\circ}$ C

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Synthesisof1,3-phenylenebis(2-(4-(4-oxo-3-((5-styryl-1,3,4-oxadiazol-2-
yl)methyl)thiazolidin-2-yl)phenoxy)acetate)yl)methyl)thiazolidin-2-yl)phenoxy)acetate)[XXII] and 1,4-phenylene bis(2-(4-(4-oxo-3-
((5-styryl-1,3,4-oxadiazol-2-yl)methyl)thiazolidin-2-yl)phenoxy)acetate)

These compounds were synthesized by using the same procedure given for synthesizing compounds[XI-XIII] and [XIV-XVI], except using the compounds [XX],[XXI]instead of compounds [V-VII] and [VIII-X]

Data compound [XXII]:brown color, Yield 63%, m.p = $125-127^{0}$ C Data compound [XXIII]: brown color , Yield 65%, m.p = $>300^{0}$ C

Results and discussion

In order to obtain the compounds [I] and [II] ,we reacted the resorcinol or hydroquinone with two moles from chloroacyl chloride in pyridine and DMF. These compounds were identified by FTIR spectroscopy.

The FTIR spectra of these compounds showed disappearance bands of the v OH groups, which were observed in the starting materials and showed new absorption stretching bands at 1774 cm⁻¹ and 1764cm⁻¹ that are attributed to the C=O of ester groups[12],respectively. Also, showed stretching band at 793cm⁻¹ and 758cm⁻¹ for CH₂Cl,respectively.

The dialdehyde [III] and [IV] were prepared from reacted compound [I] or [II]with two moles from 4-hydroxybenzylaldehyde and fused sodium acetate in absolute ethanol .The FTIR spectra of these compounds showed new stretching bands at 1686cm^{-1} and 1668 cm^{-1} assigned to CHO groups , also showed new stretching bands at 1217cm^{-1} and 1215cm^{-1} for ether groups(-CH₂-O-),respectively. While the ¹HNMR spectrum (in DMSO-d₆ as a solvent) of compound [III], Figure(1) showed: a singlet signal at δ 9.77 ppm for two protons of CHO groups, many signals in the region δ (6.17-7.75) ppm of twelve aromatic protons of benzene rings, a singlet signal at δ 3.45 ppm due to four protons of two (OCH₂CO)groups.

The Schiff bases [V-VII]and[VIII-X] were synthesized by condensation reaction of one mole from the dialdehyde compounds[III] or [IV]with different aromatic amine in ethanol. These Schiff bases were characterized by melting points and FTIR and ¹HNMR spectroscopy.

The characteristic FTIR spectra of these compounds showed the disappearance of absorption stretching bands due to NH₂ and CHO for starting material together with the appearance of stretching bandsat range (1651-1654) cm⁻¹ and (1638-1645)cm⁻¹ assignable to C=N groups, respectively. The characteristics FTIR absorption bands of new Schiff bases are listed in Table'(2). The ¹HNMR spectra (in DMSO-d₆ as a solvent) for compound [V] and [IX] showed: a singlet signals at δ 8.45 ppm and δ 8.59 ppm for two protons of azomethine (N=CH) groups, respectively, multiplet signals appear at δ (6.85-7.74)ppm and δ (6.54-7.75)ppm for twenty aromatic protons of benzene rings, respectively. A sharp signal at δ 3.75 ppmthat could be attributed to the four protons of two(OCH₂CO) groups and six protons of two (CH₃O) terminal groups for compound [V].while two protons of two(OCH₂CO) groups and six protons of two (CH₃) terminal groups for compound [IX] appear at δ 3.32 ppm and δ 2.92 ppm, respectively, the ¹HNMR spectrum of compound [V] as Figure(2).

The thiazolidin-4-one derivatives[XI-XIII] and [XIV-XVI] were synthesized by the reaction of two moles of thioglycolic acid with one mole of Schiff bases [V-VII]and [VIII-X] in dry benzene ,respectively. These compounds were characterized by their melting points and FTIR spectroscopy. The FTIR spectra showed the disappearance of a stretching band of imine groups and the appearance of a stretching band of carbonyl group of thiazolidinone moiety[13] around (1662-1678) cm⁻¹ and(1654-1685) cm⁻¹,while (C-S) groups[14] around (950-993) cm⁻¹ and (970-997) cm⁻¹,respectively. The FTIR spectral data for these compounds are listed in Table (3).¹HNMR spectra of compounds [XII] and [XIV] (in DMSO-d6 as a solvent): showed signals at δ 2.18 ppm and δ 3.65 ppm for six protons of the two (CH₃) and

(CH₃O) groups ,respectively, a singlet was observed at δ 3.65 ppm and δ 3.72 ppm for four protons of (OCH₂CO) groups ,respectively. Singlet signal appeared at δ 4.36ppm and δ 4.10ppm due to four protons of two(H-5 thiazolidinone) ,respectively. Also ,multiplet signals appear at δ (6.30-7.46)ppm and δ (6.85-7.51)ppm for twenty aromatic protons of benzene rings and two protons of two (H-2 thiazolidinone) respectively. Figure(3) showed the ¹HNMR spectrum of compound [XII].

The ester compound [XVII] was prepared from reaction of cinnamic acid in methanol with conc. H_2SO_4 (as a catalyst). The FTIR spectrum for compound [XVII] showed the disappearance of absorption stretching bands of O-H and C=O groups of (carboxylic moiety) in starting materials together with the appearance of a new stretching band at 1716cm⁻¹ assigned to C=O group of ester moiety.

The condensation of one mole of ester compound [XVII] with excess of 80% hydrazine hydrate in ethanol produced the acid hydrazide [XVIII]. The compound was characterized by FTIR spectroscopy ,the FTIR spectrum for this compound showed stretching vibration of (NH, NH₂) groups in the region (3280-3188)cm⁻¹ as well as stretching absorption at 1664cm⁻¹ of ν C=O (amide) and disappearance of absorption stretching band due to ν C=O of ester moiety.

The acid hydrazide[XVIII] and glysine compound could be smoothly cyclidehydrated by boiling in phosphorus oxychloride to produce the 1,3,4-oxadiazol compound[XIX]. The FTIR spectrum for this compound showed absorption stretching band at 1637cm⁻¹due to υ C=N group for oxadiazol ring.The mechanism[15] of dehydration in the presence of POCl₃ is depicted in the following steps: (Scheme 2)



Scheme (2)

Then, reactant the1,3,4-oxadiazol compound[XIX] with dialdehyde compound [III] or [IV] to synthesize new Schiff base compounds [XX] and [XXI], respectively. These Schiff bases were characterized by melting points and FTIR and ¹HNMR spectroscopy.

The characteristic FTIR spectra of these compounds showed the disappearance of absorption bands due to NH_2 and CHO for stretching of starting material together with the appearance of stretching bandsat $1645 \text{cm}^{-1} \text{and} 1651 \text{cm}^{-1}$ assignable to C=N groups,respectively. The ¹HNMR spectrum (in DMSO-d₆ as a solvent) for compound [XX], as Figure(4) showed: a singlet signals at $\delta 8.53$ ppm for two protons of azomethine (N=CH)

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groups ,multiplet signals appear at δ (6.40-7.75)ppm for twenty two aromatic protons of benzene rings, signals at δ (5.41-6.33) ppm that could be attributed to the four protons of two(-CH=CH-)groups. Also singlet signal appears at δ 3.51 ppm due to four protons of two (OCH₂CO) groups and signal appears at δ 2.08 ppm for four protons of two(CH₂N) groups,.

In addition to, synthesizing new thiazolidin-4-one derivatives [XXII] and [XXIII] by adding two moles of thioglycolic acid with one mole of Schiff bases [XX] and [XXI] in dry benzene as a solvent. The FTIR spectra for these compounds showed the disappearance of a stretching band of imine groups and the appearance of a stretching band of carbonyl group of thiazolidinone moiety at 1674cm⁻¹ and 1655 cm⁻¹ also C-S groups at 997 cm⁻¹ and 968cm⁻¹, respectively. The mass spectrum of compound [XXIII] that molecular weight =948, Figure (5) showed base peak at m/z=110 .Also the spectrum showed peak attributed to the presence of the oxadiazol ring (m/z=81 and 53) and peak at (m/z=149)of the thiazolidin-4-one ring ,as while as peaks at m/z= 77 and 65 for aromaticity of this compound. The fragments of this compound were illustrated in Scheme (3).



Liquid crystalline properties

The liquid crystalline properties were investigated by polarized optical microscopy (POM) in association with differential scanning calorimetry(DSC).

All the schiff bases compounds [V-X] showed liquid crystals phases. The compound [V]showed monotropic droplets nematic texture under POM because the methoxy groups have a higher polarizability, this could be explained in term of terminal/lateral (t/l) interaction forces ratio, because the methoxy chain led to a higher ratio of t/l interaction forces and when this ratio is high, compound tend to give less ordered mesophases (nematic mesophase)[16] as Figure 6(a),while Figure(7) showed DSC thermogram for this compound.

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The compounds [VII] and [X] showed enantiotropic SmA phase as Figure 6(b) for compound [VII].Butthe compounds [VI],[VIII] and [IX] showed enantiotropic SmB phase[17] as Figures 6(c) and 6(d) for compounds [VIII] and [IX] ,respectively.

Finally, all thiazolidin-4-one derivatives[XI-XIII],[XIV-XVI]and [XXIII] didn't show any liquid crystals properties but simply changes from the crystalline solid state to the isotropic liquid except the compound [XXII] showed nematic phase ,this is may by presence of oxadiazole ring and geometric structure of this compound. The transition temperatures for Schiff bases compounds [V-X] and thiazolidin-4-one derivatives[XI-XIII],[XIV-XVI], [XXII]and compound [XXIII] are summarized in Table 4 and Table5, respectively.

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Table (1): The physical properties for the operation	compounds[V-XVI]
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Comp . No.	X	Nomenclature	Molecular formula	Yield %	М. Р ⁰ С	Color
[V]	CH ₃ O	1,3-phenylene bis(2-(4-((4- methoxyphenylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_8$	85	212- 214	gold
[VI]	CH ₃	1,3-phenylene bis(2-(4-((p- tolylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_6$	87	203- 205	Yellow
[VII]	ОН	1,3-phenylene bis(2-(4-((4- hydroxyphenylimino)methyl)phenoxy)acetate)	$C_{36}H_{28}N_2O_8$	73	65- 67	brown
[VIII]	CH ₃ O	1,4-phenylene bis(2-(4-((4- methoxyphenylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_8$	82	190- 192	gold
[IX]	CH ₃	1,4-phenylene bis(2-(4-((p- tolylimino)methyl)phenoxy)acetate)	$C_{38}H_{32}N_2O_6$	75	209- 211	brown
[X]	ОН	1,4-phenylene bis(2-(4-((4- hydroxyphenylimino)methyl)phenoxy)acetate)	$C_{36}H_{28}N_2O_8$	86	>30 0	dark brown
[XI]	CH ₃ O	1,3-phenylene bis(2-(4-(3-(4-methoxyphenyl)- 4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_{10}S_2$	82	gum my	Pal yellow
[XII]	CH ₃	1,3-phenylene bis(2-(4-(4-oxo-3-p- tolylthiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_8S_2$	72	gum my	Pal yellow
[XIII]	ОН	1,3-phenylene bis(2-(4-(3-(4-hydroxyphenyl)- 4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{40}H_{32}N_2O_{10}S_2$	68	gum my	brown
[XIV]	CH ₃ O	1,4-phenylene bis(2-(4-(3-(4-methoxyphenyl)- 4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_{10}S_2$	62	170- 172	Off white
[XV]	CH ₃	1,4-phenylene bis(2-(4-(4-oxo-3-p- tolylthiazolidin-2-yl)phenoxy)acetate)	$C_{42}H_{36}N_2O_8S_2$	67	gum my	brown
[XVI]	ОН	1,4-phenylene bis(2-(4-(3-(4-hydroxyphenyl)- 4-oxothiazolidin-2-yl)phenoxy)acetate)	$C_{40}H_{32}N_2O_{10}S_2$	74	133- 135	brown

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G	Characteristic bands FTIR spectra(cm ⁻¹)					
Comp. No.	U(O-H)	U(C-H)	U(C-H)	U(C=O)	U(C=N)	U (C=C)
		aromatic	aliphatic	ester		aromatic
[V]	_	3003	2970-2841	1741	1653	1606
[VI]	_	3026	2970-2866	1732	1654	1604
[VII]	3415	3070	2966-2858	1707	1651	1604
[VIII]	_	3005	2972-2839	1720	1645	1606
[IX]	_	3026	2978-2866	1730	1640	1606
[X]	3415	3051	2981-2823	1714	1638	1608

Table (2): Characteristics FTIR absorption bands of compounds[V-X]

Table (3):Characteristics FTIR absorption bands of thiazoldin-4-ones [XI-XVI]

	Characteristic bands FTIR spectra(cm ⁻¹)				
Comp. No.	U(C-H)	U(C-H)	U(C=O)	U(C=C)	U(C-S)
110.	aromatic	aliphatic	thiazoldinone	aromatic	
[XI]	3095	2962-2833	1662	1603	950
[XII]	3030	2958-2858	1678	1608	964
[XIII]	3068	2962-2806	1678	1604	993
[XIV]	3010	2956-2837	1654	1600	970
[XV]	3030	2970-2830	1685	1608	997
[XVI]	3010	2966-2852	1681	1600	995

Comp. No.	Transition Temperatures (°C)
[V]	$Cr \xrightarrow{201} N \xrightarrow{224} I$
[VI]	$Cr \xrightarrow{175} SmB \xrightarrow{200} N \xrightarrow{220} I$
[VII]	$Cr \xrightarrow{150} SmA \xrightarrow{185} N \xrightarrow{209} I$
[VIII]	$Cr \xrightarrow{160} SmB \xrightarrow{205} N \xrightarrow{225} I$
[IX]	$Cr \xrightarrow{175} SmB \xrightarrow{220} N \xrightarrow{233} I$
[X]	$Cr \stackrel{120}{\longleftarrow} SmA \stackrel{160}{\longleftarrow} N \stackrel{200}{\longleftarrow} I$

Cr, crystalline phase;SmB smectic B phase ;SmA smecticA phase; N, nematic phase; I, isotropic liquid

Table (5): Phase transition temperatures (°C) of thiazolidin-4-one derivatives [XI-
XIII],[XIV-XVI], [XXII]and compound [XXIII]

Comp. No.	Transition Temperatures (°C)
[XI]	$Cr \xrightarrow{170} I$
[XII]	$Cr \xrightarrow{150} I$
[XIII]	$Cr \xrightarrow{160} I$
[XIV]	Cr <u>179</u> ► I
[XV]	$Cr \xrightarrow{165} I$
[XVI]	$Cr \xrightarrow{140} I$
[XXII]	$Cr \xrightarrow{110} N \xrightarrow{175} I$
[XXIII]	$Cr \xrightarrow{310} I$

Cr, crystalline phase ;N, nematic phase; I, isotropic liquid



Figure (1):The ¹HNMR spectrum of compound [III]



Figure(2):The ¹HNMR spectrum of compound [V]



Figure (3):The ¹HNMR spectrum of compound [XII]



Figure (4):The ¹HNMR spectrum of compound [XX]



Figure (5): The mass spectrum of compound [XXIII]

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Figure(6):Cross polarizing optical textures of (a) nematicphase for compound [V] at 210 $^{\circ}$ C(b)smectic A phase for compound [VII] at170 $^{\circ}$ C(c)smecticB phase for compound [VIII] at 190 $^{\circ}$ C (d) smectic B phase for compound [IX] at 210 $^{\circ}$ C



Figure (7) : DSC thermogram for compound [V]

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