



Synthesis, Characterization and Investigation Liquid Crystalline, Properties of 1, 2, 3-triazole Derivatives via Cycloaddition Reaction

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Abstract

The new of compounds synthesized by sequence reactions starting from a reaction of 3-phenylenediamine or 4-phenylenediamine with chloroacetyl chloride to produce the compounds [I]_{a,b}, then the compounds [I]_{a,b} reacted with sodium azide to yield compounds [II]_{a,b} that reacted 1,3-dipolar cycloaddition reaction with acrylic acid to give compounds [III]_{a,b} these compounds reacted with methanol led to ester compounds [IV]_{a,b} then reacted with hydrazine to give acid hydrazide [V]_{a,b}. Finally compounds [V]_{a,b} reacted with aromatic aldehydes to product shiff bases derivatives. The compounds characterized by mp. , IR, ¹H NMR in addition to mass spectroscopy for some of them the liquid crystals properties were studied by using polarized optical microscope (pom) and deferential calorimetry (DSC).

Keywords: *Liquid crystal, 1, 2, 3-triazole ring, Clicks reaction.*

Introduction

Many workers developed liquid crystal with adding heterocyclic to the structures of these compounds because heterocyclic compounds are used in many applications [1]. The mesogenic compounds with heterocyclic have been development [2, 3]. We found some of the bent heterocyclic mesogene, for example furane, oxadiazole, thidiazole, and benzimidazole derivatives containing hetero ring as terminally group these compounds display liquid crystal properties [4].

This study synthesized of new compounds which have a five-membered 1, 2, 3-triazole ring the derivatives with [1,2,3]-triazole ring, can synthesized via copper catalyzed by dipolar cycloaddition reaction the terminal alkenes and azides, this name Click reaction this attention in the field of organometallic [5], organic chemistry [6] bio conjugations [7] pharmacist [8], from literature, few mesogenes synthesized containing [1,2,3]-triazole ring [9].

The calamitic mesogenes with [1,2,3]-triazole ring and alkyl chains as a terminal group

were display liquid crystalline properties [10,11].

For this the aim of this work synthesized new derivatives containing [1,2,3] triazole and studied liquid crystalline behavior.

Experimental

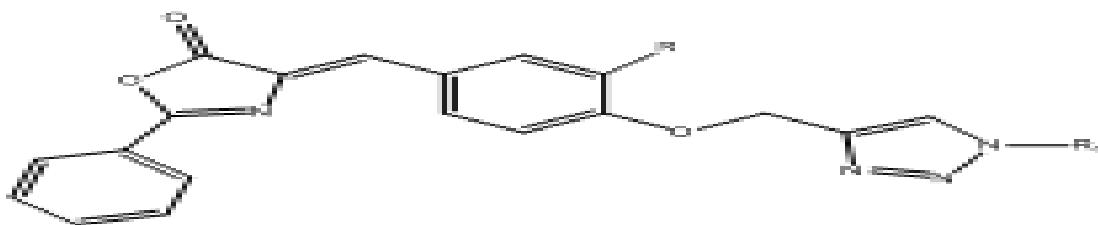
Materials

Materials were obtained from Aldrich and Merck, Fluka all starting chemical.

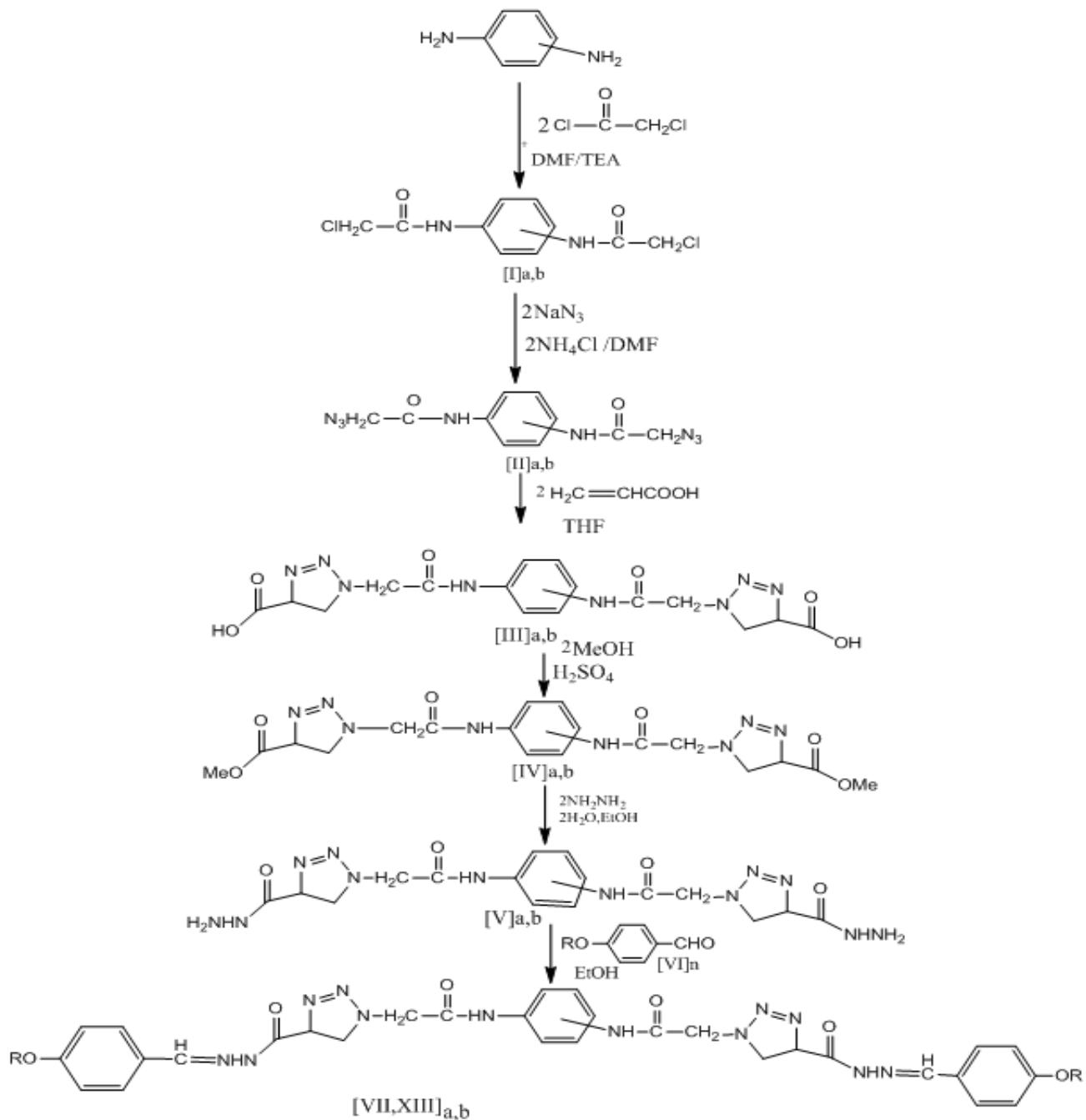
Instrumentals

FTIR spectra measurement by (KBr) on a Shimadzu (IR Affinity-1) FTIR spectroscopy. Diyala University H1 NMR determined by company: Burker 300 MHz, origin: Switzerland in DMSO with TMS, measurements made at chemistry department asfahan of University. Mp. were measured by, Gallenkamp apparatus. Phase's temperatures and types of the mesophases studied by POM modelleica DM2500 m and DSC measurements were conducted with STA PT-1000LINSIS

Synthesis



The scheme 1: Show synthesis all compounds



R= C_nH_{2n+1}

Scheme (1)

Synthesis of N,N-(1,3-Phenylene) bis (2-chloroacetamide)[I]_a and N,N- (1,4-Phenylene) bis (2-chloroacetamide) [I]_b

A mixture of 1, 3-phenylenediamine or 1, 4-phenylenediamine (1.08gm , 0.01mol), in DMF (3 ml) then addition triethylamine (4ml) and chloroacetyl chloride (2.26gm , 0.02mol) was refluxed for (6 hrs). After cooling the mixture addition to water ice then filtration dried and recrystallized from ethanol .The compound [I]_a , color of white, yield 76%, m.p = 261 C° the compound [I]_b , color of grey , yield 72%, m.p=271C°

Synthesis of N,N-(1,3-phenylene)bis(2-azidoacetamide) [II]_a and N,N-(1,4-phenylene) bis (2-azidoacetamide) [II]_b

To a solution of compounds [I]_a and [I]_b (0.001mol) in 3ml DMF added Sodium azide (0.13 gm, 0.002 mol) then added ammonium chloride (0.106gm , 0.002mol) and stirring and the mixture refluxed for (4hrs) then resulting solution cool then added in water ice and the product obtained collected. The compound [II]_a , color of brown, yield 76%, m. p =211C° the compound [II]_b , color of dark red , yield 72% , m.p =229C°

Synthesis of 1,1-((1,3-phenylene)bis (azanediyl))bis (2-oxoethane-2,1-diyl) bis (4,5-dihydro-1H-1,2,3-triazole-4-carboxylic acid) [III]_a and 1,1- ((1,4-phenylene)bis (azanediyl)) bis (2-oxoethane-2,1-diyl)bis (4,5-dihydro-1H-1,2,3-triazole-4-carboxylic acid) [III]_b

In DMF (3ml) were added compound [III]_a and [III]_b (0.05gm , 0.0002 mol) and added acryli acid (0.028gm , 0.0004mol) refluxed for (24hrs) then under reduced pressure solvent evaporated and the precipeted was dried The compound [III]_a , color of pink , yield 81%, m. p =131C° the compound [III]_b , color of purple , yield 70% , m.p =142 °C

Synthesis of Dimethyl1,1-((1,3-phenylene) bis (azanediyl)) bis (2-oxoethane-2,1-diyl) bis (4,5-dihydro-1H-1,2,3-triazole-4-Carboxylate) [IV]_a and dimethyl1,1((1phenylene)bis(azanediyl)) bis (2-oxoethane-2,1-diyl) bis (4,5-dihydro-1H-1,2,3-triazole-4-carboxylate) [IV]_b

In absolute methanol (100ml) were added compound [IV]_a and [IV]_b (102.8 gm, 0.246 mol) then added (3ml) sulfuric acid refluxed for (6 hrs) the mixture was cooled at room temperature then added solution sodium be carbname 5% the precipeted washing in water

The compound [IV]_a , color of roan , yield 72% , m.p =217C° the compound [VI]_b , color of black , yield 76% , m.p =225C°

Synthesis of N,N-(1,3-phenylene)bis (2-(4-hydrazinecarbonyl) 4,5-dihydro-1H1,2,3-triazole-1yl) acetamide [V]_aand N,N-(1,4-phenylene)bis(2-(4-hydrazinecarbonyl) 4,5-dihydro-1H1,2,3-triazole-1yl) acetamide [V]_b

To compound [IV]_a and [IV]_b (2.67gm , 0.006mol) added (3ml) of hydrazine 80% then added (5ml) absolute ethanol the reaction mixture was refluxed for (3hrs) then resulting solution was allowed to cool to room temperature , and recrystallized from ethanol The compound [IV]_a , color of brown , yield 68% , m. p =237C° the compound [IV]_b , color of dark brown, yield 76% , m.p =225C°

Synthesis of 4-alkoxybenzaldehyde [VI] n

To a solution of potassium hydroxide(4.87gm , 0,087mol in absolute ethanol 50 ml added (10.6gm , 0,087mol of 4-hydroxybenzaldehyde then added (0.13mol) alkyl bromide the reaction mixture was refluxed for (6hrs) then added 50ml water. The product was extracted by using ethyl ether (50ml) organic layer washed in (25ml) solution sodium hydroxide 10% then (25ml) water, after that the solvent was evaporated to product the compounds [VI]_n.

Synthesis of N,N-((1,3 -phenylene)bis (2-(4-(2(4-methoxy benzylidene) hydrazine-1-carbonyl) 4,5-dihydro-1H-1,2,3-triazol-1-yl) acetamide)[VII]_a and N,N-((1,4 phenylene) bis (2-(4-(2(4-methoxybenzylidene) hydrazine-1-carbonyl) 4,5-dihydro-1H-1,2,3-triazol-1-yl) acetamide) [VII]_b

A mixture of compound [VIII]_a and [VIII]_b (0.446gm , 0.001mol) with 4-alkoxybenzaldehydecound [VI]_n (0.002mol)then (5ml) absolute ethanol the solution heating for (3-4hrs) then cooled after that filtered the physical properties for these compounds we listed in Table (1)

Results and Discussion

The compound [I]_a and [I]_b were prepared from reaction m-phenylene diamine and p-phenylene diamine with two moles of chloroacetyl chloride in DMF and TEA. The FTIR spectra for these compounds showed the disappearance of bands of (NH₂)in starting materials with appearance band sat 1656cm⁻¹ and assigned to C=O amide groups

,respectively . The reaction of one mole of compound [I]_a and [I]_b with two moles of sodium azide and ammonium chloride in DMF produced compounds [II]_a and [II]_b. That characterized by FTIR spectroscopy where FTIR spectra of these compounds showed stretching vibration in 2113cm⁻¹and 2135cm⁻¹ for (N≡N). ¹HNMR spectrum (DMSO-d 6) for compound [II] b display: a single t signals at 810.14ppm for two protons of N-H groups, signals appear at δ 6. 58-7.96 ppm for four protons of benzene ring and a signal at δ 4.03 ppm for four protons of two CH₂ groups .The compounds [III]_a and [III]_b product from reaction two moles of acrylic acid with compound [II]_a and [II]_b.

The FTIR spectra of these compounds appearance bands at 1743cm⁻¹ and 1723cm⁻¹ assigned to C=O carboxylgrous with disappearance of absorption stretching bands of (N≡N) groups for starting materials ,this is a good evidence for cyclization of 1,2,3-triazole ring the ester compounds [IV]_{a,b} formation from reaction compound [III]_{a,b} with absolute methanol in sulfuric acid (as a catalyst) The FTIR spectra showed disappearance of bands of COO and OH 1743cm⁻¹ and 3432cm⁻¹ carboxylic acid and showed stretching bands at 1688 for carbonyl C=O for ester groups. While reacting the later compounds with hydrazine hydrate product acid hydrazide [V]_{a,b}

The FTIR spectra showed stretching vibration to asymmetric and symmetric bands of (NH-NH₂) in the region (3429-3229)cm⁻¹ and 3418cm⁻¹ – 3216 cm⁻¹ stretching bands at 1649 cm⁻¹ to C=O amide groups, respectively. The ¹HNMR spectrum for compound [V]_b showed: signal at δ 10.12ppm for two protons NH of (-NHCONH-) groups ,singlet signal at δ 8.82 ppm for 2 NH of acid hydrazide , many signals at region δ (7.91-8.38) ppm for four protons of aromatic protons , also showed douplat signal of δ 7.74 ppm for protons CH₂ of (C₅) of triazole rings , as while as showed triplet signal at δ 7,58 ppm for protons (CH) of C₄ of triazole rings^[12] . Also showed signal at 85.44ppm for four protons of (NH₂) groups.

Finally singlet signal atδ 3.33 ppm for four protons of (-COCH₂) groups. The Schiff bases compounds [VII-XIII]_{a,b} synthesized by reaction acid hydrazide [V]_{a,b} with different aromatic aldehyde. The ¹HNMR spectrum for compound [VII-XIII]_{a,b} showed: singlet signal at δ 10.12ppm for two protons NH of amide groups, many signals at region δ(7.91-8.38) ppm for four protons of aromatic protons, also showed douplat signal of δ 7.74 ppm for protons CH₂ of (C₅) of triazole rings, as while as showed triplet signal at δ 7,58 ppm for protons (CH) of C₄ of triazole rings^[12]. Also singlet signal at δ 3.33 ppm for 4 H of (-COCH₂) groups .The characterization FTIR absorption bands for these compounds are listed in Table (1).

Table 1: The physical properties for compounds [VII-XIII]_{a,b}

No.	Name	M.P.(°C)	% Yield
[VII] _a	N,N'-(1,-phenylene)bis(2-(4-(2-(4-methoxybenzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	173	75
[VII] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-methoxybenzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	181	69
[VIII] _a	N,N'-(1,3-phenylene)bis(2-(4-(2-(4-ethoxybenzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	175	72
[VIII] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-ethoxybenzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	187	80
[IX] _a	N,N'-(1,3-phenylene)bis(2-(4-(2-(4-propoxybenzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	190	67
[IX] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-propoxybenzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	197	73
[X] _a	N,N'-(1,3-phenylene)bis(2-(4-(2-(4-pentyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	201	88
[X] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-pentyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	209	81
[XI] _a	N,N'-(1,3-phenylene)bis(2-(4-(2-(4-hexyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	211	76
[XI] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-hexyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	218	65
[XII] _a	N,N'-(1,3-phenylene)bis(2-(4-(2-(4-heptyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	223	74
[XII] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-heptyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	229	66
[XIII] _a	N,N'-(1,3-phenylene)bis(2-(4-(2-(4-octyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	237	82
[XIII] _b	N,N'-(1,4-phenylene)bis(2-(4-(2-(4-octyloxy)benzylidene)hydrazine-1-carbonyl)-4,5-(dihydro-1H-1,2,3-triazol-1-yl)acetamide	246	79

Table 2: the characterization FTIR absorption bands of compounds [VII-XIII]_{a,b}

COMP	v N-H	.v C-H arom	v C-H aliph	v C=O	v C=Cothers
[VII] _a	3267	3087	2927-2839	1664	1600
[VII] _b	3287	3051	2927-2837	1662	1598
[VIII] _a	3296	3034	2929-2856	1656	1618
[VIII] _b	3262	3062	2937-2893	1643	1600
[IX] _a	3290	3043	2916-2881	1656	1604
[IX] _b	3298	3043	2926-2881	1656	1604
[X] _a	3270	3043	2951-2866	1656	1602
[X] _b	3276	3051	2943-2866	1662	1604
[XI] _a	3294	3057	2945-2862	1670	1606
[XI] _b	3284	3043	2926-2858	1685	1604
[XII] _a	3285	3079	2926-2862	1641	1618
[XII] _b	3263	3042	2981-2937	1620	1600
[XIII] _a	3285	3079	2922-2852	1641	1614
[XIII] _b	3308- 3282	3063	2920-2850	1659	1604

Mesomorphic Behavior

The temperatures and texture mesophase studied by polarizing optical microscopy (POM) and by differential scanning calorimetry (DSC). Transition temperatures for two series [VII-XIII]_a and [VII-XIII]_b were summarized in Table (3). The compounds [VII]_a, [VIII]_{a,b}, [IX]_{a,b}, [X]_{a,b} and [XI]_{a,b} showed only nematic texture on heating and cooling under polarizing optical microscopy as Fig. 1(a) for compound [VII]_a and Fig. 1(b) for compound [XI]_b, but compound [VII]_b didn't show any liquid crystalline properties but simply change from crystal to isotropic liquid, the DSC thermo gram of compound [VII]_a as in Figure (2). While the compounds [XII]_a and [XIII]_b showed dimorphism

smectic phase Sm A besides to nematic phase N, also the compound [XIII]_a showed smectic phase SmB and nematic phase as Fig 1(c) for compound [XIII]_a and Fig. 1(d) droplets nematic phase of compound [XIII]_b. In addition to, the compound [XII]_b showed only smectic phase Sm A. The Fig. (3) showed DSC thermo gram of compound [XIII]_b. This behavior can be attributed to the chain length of alkoxy terminal group that interferes with liquid crystalline ordering, When the ratio of terminal/lateral (t/l) interaction is high, compounds give less ordered mesophases (nematicmesophase), while when this ratio is low, the compounds give high order mesophases (smectic phase)^[13]

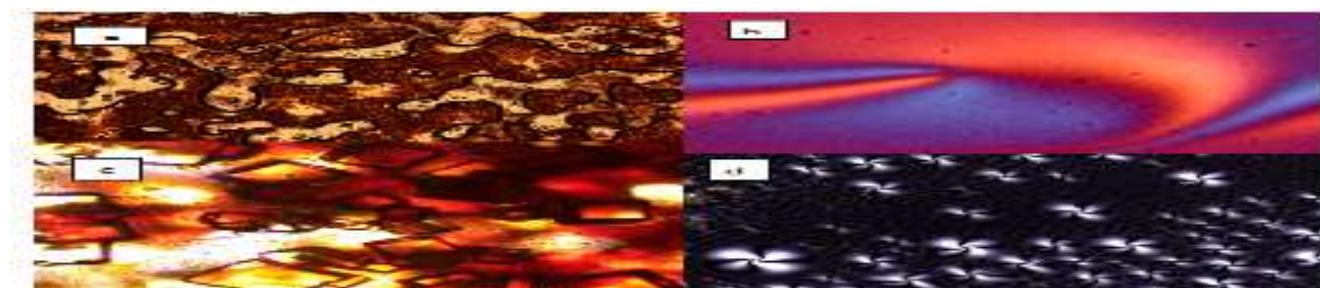


Figure 1: Cross polarizing optical textures of (a) Nematic thread-like texture. For compound [VII]_a at 198°C (b) schlieren-nematic phase for compound [XI]_b at 183°C (c) smectic B phase for compound [XIII]_a at 120°C (d) droplet nematic phase for compound [XIII]_b at 290°C

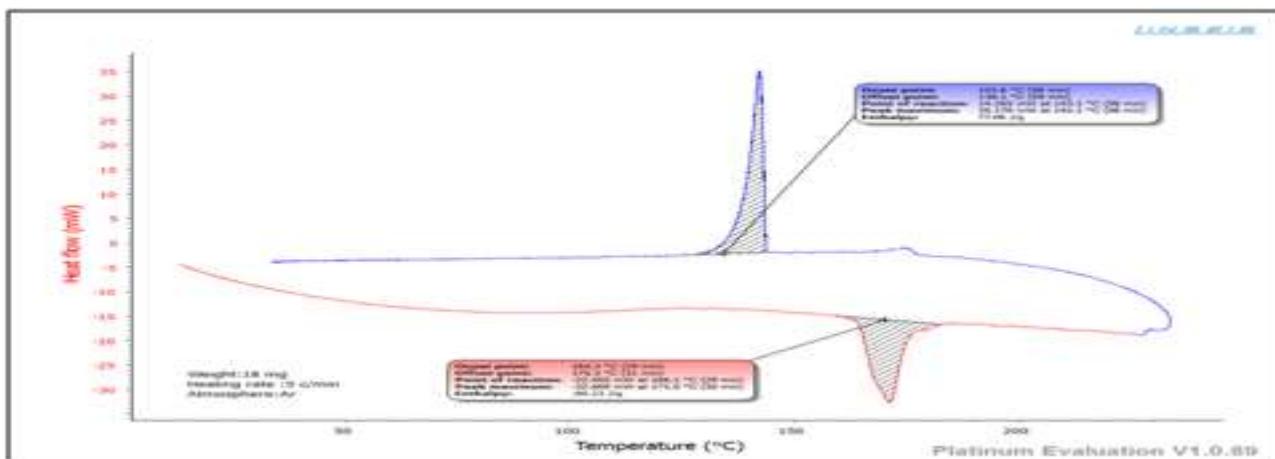


Figure 2: DSC thermo gram of compound [VII]a

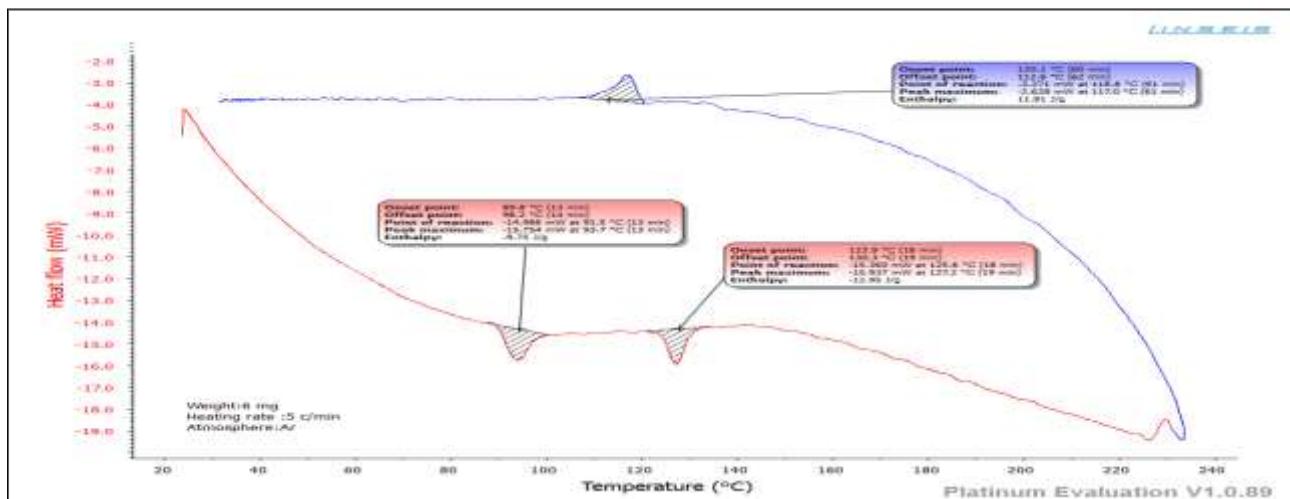


Figure 3: DSC thermo gram of compound [XIII]b

Table 3: the phase transition temperatures of series [VII-XIII] a and [VII-XIII]b

Compound	Phase transition	Compound	Phase transition
[VII] _a	$\text{Cr} \xrightleftharpoons[140]{162} \text{N}$ $\text{N} \xrightleftharpoons{230} \text{I}$	[VII] _b	$\text{Cr} \xrightarrow{\text{Mn} > \text{C}} \text{I}$
[VIII] _a	$\text{Cr} \xrightleftharpoons[250]{180} \text{N}$ $\text{N} \xrightleftharpoons{} \text{I}$	[VIII] _b	$\text{Cr} \xrightleftharpoons{165} \text{N}$ $\text{N} \xrightleftharpoons{205} \text{I}$
[IX] _a	$\text{Cr} \xrightleftharpoons[171]{140} \text{N}$ $\text{N} \xrightleftharpoons{} \text{I}$	[IX] _b	$\text{Cr} \xrightleftharpoons{180} \text{N}$ $\text{N} \xrightleftharpoons{160} \text{I}$
[X] _a	$\text{Cr} \xrightleftharpoons[185]{160} \text{N}$ $\text{N} \xrightleftharpoons{} \text{I}$	[X] _b	$\text{Cr} \xrightleftharpoons{135} \text{N}$ $\text{N} \xrightleftharpoons{160} \text{I}$
[XI] _a	$\text{Cr} \xrightleftharpoons[204]{183} \text{N}$ $\text{N} \xrightleftharpoons{} \text{I}$	[XI] _b	$\text{Cr} \xrightleftharpoons{150} \text{N}$ $\text{N} \xrightleftharpoons{198} \text{I}$
[XII] _a	$\text{Cr} \xrightleftharpoons{196} \text{SmA}$ $\text{SmA} \xrightleftharpoons[225]{260} \text{N}$ $\text{N} \xrightleftharpoons{} \text{I}$	[XII] _b	$\text{Cr} \xrightleftharpoons{110} \text{SmA}$ $\text{SmA} \xrightleftharpoons{160} \text{I}$

[XIII] _a	$\text{Cr} \xrightleftharpoons{75} \text{SmB}$ $\text{SmB} \xrightleftharpoons{105} \text{N}$ $\text{N} \xrightleftharpoons{125} \text{I}$	[XIII] _b	$\text{Cr} \xrightleftharpoons[116]{94} \text{SmA}$ $\text{SmA} \xrightarrow{172} \text{N}$ $\text{N} \xrightarrow{234} \text{I}$

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