

Synthesis, Characterization and Study of Liquid Crystalline Behavior of New Compounds Containing Thiazolidin-4-one, 1, 2, 3-Triazole and Benzimidazol Rings

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Abstracts

All new compounds synthesized by many reactions starting from a product the compounds [I]_{a,b} from reaction of 3-phenylenediamine or 4-phenylenediamine with chloroacetyl chloride, then the compounds [I]_{a,b} reacted with potassium thiocyanate to yield compounds [II]_{a,b}. While the compounds [III]_{a,b} yield from reacted the compounds [I]_{a,b} with sodium azide then the compounds [III]_{a,b} reacted 1,3-dipolar cycloaddition reaction with acrylic acid to give compounds [IV]_{a,b} and the later compounds reacted with phenylene diamine to product benzimidazole compounds [V]_{a,b}. In addition to synthesized acid chloride compounds [VI]_{a,b} by reacted the compounds [IV]_{a,b} with thionyl chloride. Finally reacted the compounds [VI]_{a,b} with different aromatic amines to give amide compounds [VII-X]_{a,b}. The synthesized derivatives characterized viamp. , FTIR, ¹HNMR in addition to mass spectroscopy. The liquid crystals properties were studied by using polarized optical microscope (POM) and differential scanning calorimetry(DSC).

Keywords: *liquid crystal; benzimidazol; thiazolidin-4-one.*

Introduction

Many methods in literatures for preparation of 1,2,3- triazole compounds including cyclization of azido acetamide compounds [1-6] by 1,3-dipolar cycloaddition reaction [7,8]. Large number of 1,2,3-triazoles synthesized via 1,3-dipolarcycloadditionsorganic azides and acrylic acid with azides.

In generally, the cycloaddition reaction when the acrylic acid which have electron withdrawing was faster but on azides the effect of these groups have the opposite, also the bulky substituent's hinder the reaction, but butter the selectivity [9].

Avail synthesized of liquid crystal with hetero rings have a wide area in the recent years because of their photochemical and optical properties [10] In 1922 the Friedel called the "mesomorphic states of matter [11] in his scientific assessment of observations of the so-called liquid crystals.

The less important when synthesized liquid crystal derivatives containing other than six member rings this duo to the bent and less showed liquid crystalline behavior. It was substantial to design molecules that appear liquid crystal properties this can involve theoretical and practical [12-13]. In recent years, successfully synthesized many mesogenes with five member hetero rings [14-16].

Materials and Methods

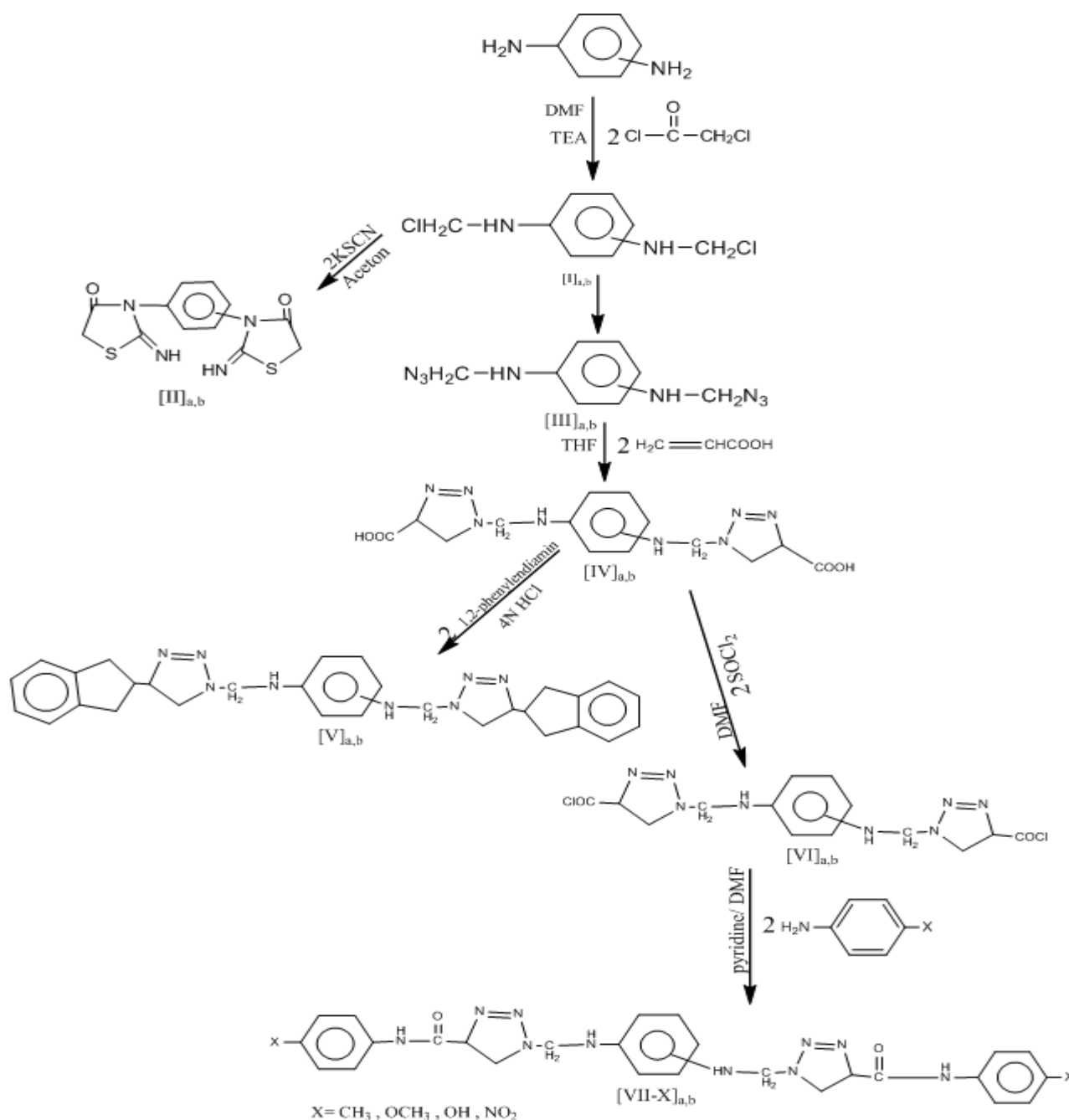
Were obtained from Riedal-deHaën and, Fluka, Merck all starting chemical

Techniques

Melting points of all the compounds measurement via Gallenkamp melting point. The FTIR spectra determined by KBr in a Shimadzu (IR Affinity-1). ¹HNMR spectra measurement via company: Burkert, 300MHz, origin: Switzerl the reported in ppm (δ) and

solvent DMSO with TMS, measurements made at chemistry department asfahan of University. The type of liquid crystal phases and their Temperatures measurement via

POM type leica DM2500 m and DSC measurements were conducted with STA PT-1000LINSIS.



All derivatives synthesized represented in scheme (1)

Synthesis

Synthesis 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 (0.18gm, 0.001mol), in DMF (2 mL) then addition triethyl amine (3ml) and chloroacetyl chloride (0.226gm, 0.002 mol) stirring for (5hrs). Then added water ice after that filtration dried and recrystallized from ethanol The compound

[I]_a, color of white, yield 76%, m.p = 212-214°C^o. The compound [I]_b, color of grey, yield 72%, m.p = 315-317°C^o

Synthesis of 3, 3-(1,3- Phenylene) Bis (2-Iminothiazolidine- 4 one) [II]_a and 3,3-(1,4-Phenylene) Bis (2-Iminothiazolidine-4 one) [II]_b

To a solution of compounds [I]_a or [I]_b (0.78gm, 0.003mol) and (5ml) acetone added (1.16gm, 0.006mol) of potassium thiocyanate, the mixture was refluxed for (3-4hrs) then under

reduced pressure solvent evaporated dried and recrystallized from ethano .

The compound [II]_a , color of crimson , yield 81%, m.p = 243C°.The compound [II]_b , color of dark red , yield 78% , m.p =281C°.

Synthesis of N,N-(1,3-Phenylene) Bis (2-Azidoacetamide) [III]_a and N,N-(1,4-Phenylene) Bis (2-Azidoacetamide) [III]_b

To a solution of compounds [I]_a and [I]_b (0.001mol) in 3ml DMF added Sodium azide (0.13gm , 0.002mol) then added ammonium chloride (0.106gm , 0.002mol) and stirring and the mixture refluxed for (4hrs) then resulting solution was allowed to cool to room temperature then added in water ice and the solid obtained was filtered dried and recrystallized from ethanol . The compound [II]_a, color of brown , yield 76% , m.p =122C° The compound [II]_b , color of dark red , yield 72% , m.p =131C°

Synthesis of 1, 1- ((1, 3-Phenynebis (Azanediyl)) bis (2- Oxoethane-2,1-diyl)Bis (4, 5-Dihydro-1H-1,2,3-Triazole-4-Carboxylic acid) [IV]_a and 1,1-((1,4-Phenyne bis (Azanediyl)) Bis (2-Oxoethane-2,1-Diyl) Bis (4,5-Dihydro-1H-1, 2, 3-Triazole-4-Carboxylic acid) [IV]_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 [IV]_a , color of pink , yield 81%, m.p =218C°. The compound [IV]_b , color of purple , yield 70% , m.p =287C°.

Synthesis of N,N-1, 3-Phenylene) Bis (2-(4-(1H-Benzo[d] Imidazol- 2-yl) -4,5-Dihydro-1H-1,2,3-Triazol-1-yl) Acetamide [V]_a, b and N,N-1, 3- Phenylene) Bis (2-(4-(1H-Benzo [d] Imidazol-2-yl)-4,5-

Dihydro-1H- 1, 2, 3- Triazol-1-yl) Acetamide [V]_a,b

To compound [IV]_a and [IV]_b (0.418gm , 0.001mol) added (3ml) of DMF then added (0.216gm , 0.002mol) of o-phenylene diamine refluxed (10hrs) .The mixture added drops of ammonia the precipeted was dried.

The compound [V]_a, color of brown, yield 77%, m.p =251Co.

The compound [V]_b, color of purple, yield 72%, m.p =274Co.

Synthesis of 1,1-((1,3 Phenynebis (Azanediyl)) Bis (2-Oxoethane-2,1-diyl))Bis(4,5-Dihydro-1H-1,2,3-Triazole-4-Carbonyl Chloride) [VI] and 1,1-((1,3 Phenynebis (Azanediyl)) Bis (2-Oxoethane-2,1-diyl)) Bis (4,5-Dihydro-1H-1,2,3-triazole-4-Carbonyl Chloride) [VI]

To a solution of compounds[V]_a and [V]_b (0.3gm, 0.0007mol) and(3ml) DMF added (0.16gm , 0.0014 mol) of thionyl chloride the reaction mixture was refluxed for (3hrs) then resulting solution was allowed to cool to room temperature and recrystallized from ethanol.

The compound [X]_a, color of off white, yield 67%, m.p =221Co.

The compound [X]_b, color of purple, yield 64%, m.p =239Co.

Synthesis of4

To a mixture of (1ml) of pyridine and (2ml) of DMF added aromatic amine and put in round flask then added compound [VI]_a and [VI]_bin bath ice and stirrer for(4hrs) and added hydrochloric acid (10%) then filtered and washing in water dried and recrystallized from ethanol, the physical properties for these compounds we listed in Table (1).

Table 1: the physical properties for compounds [VII-XIII] a, b

No.	Naem	M.P.(°C)	% Yield
[VII] _a	phenylenebis(azanediyl))bis(methylene))bis(N-(p-tolyl)-4,5-dihydro-1H-1,1,1'-((1,3-(1,2,3-triazole-4-carboxamide	198	73
[VII] _b	phenylenebis(azanediyl))bis(methylene))bis(N-(p-tolyl)-4,5-dihydro-1H-1,1,1'-((1,4-1,2,3-triazole-4-carboxamide	201	69
[VIII] _a	1,1'-((1,3-phenylenebis(azanediyl))bis(methylene))bis(N-(4-methoxyphenyl)-4,5-(dihydro-1H-1,2,3-triazole-4-carboxamide	187	67
[VIII] _b	1,1'-((1,4-phenylenebis(azanediyl))bis(methylene))bis(N-(4-methoxyphenyl)-4,5-dihydro-1H-1,2,3-triazole-4-carboxamide	192	71
[IX] _a	1,1'-((1,3-phenylenebis(azanediyl))bis(methylene))bis(N-(4-hydroxyphenyl)-4,5-dihydro-1H-1,2,3-triazole-4-carboxamide	196	68
[IX] _b	1,1'-((1,4-phenylenebis(azanediyl))bis(methylene))bis(N-(4-hydroxyphenyl)-4,5-(dihydro-1H-1,2,3-triazole-4-carboxamide	214	81
[X] _a	1,1'-((1,3-phenylenebis(azanediyl))bis(methylene))bis(N-(4-nitrophenyl)-4,5-dihydro-1H-1,2,3-triazole-4-carboxamide	206	74
[X] _b	1,1'-((1,4-phenylenebis(azanediyl))bis(methylene))bis(N-(4-nitrophenyl)-4,5-dihydro-1H-1,2,3-triazole-4-carboxamide	214	71

Results and Discussion

The compound [I]_a and [I]_b were prepared from reaction 1, 3-phenylenediamine and 1,4-phenylenediamine with two moles of chloroacetyl chloride in DMF and TEA. The FTIR spectra for these compounds display absence bands of (NH₂) in starting materials with appearance bands at 1678cm⁻¹ and 1684 assigned to C=O amide groups, respectively. The reaction of one mole of compound [I]_a and [I]_b with two moles of potassium thiocyanate and acetone produced compounds [II]_a and [II]_b.

That characterized by FTIR spectroscopy where FTIR spectra of these compounds showed stretching vibration in 1662cm⁻¹ and 1671cm⁻¹ for carbonyl group(C=O). and 698-736 cm⁻¹ for (C-S) and 1622 cm⁻¹ for (C=NH). The compounds [III]_a and [III]_b product from reaction two moles of sodium azide and two moles of ammonium chloride with compound [I]_a and [I]_b. That characterized by FTIR spectroscopy where FTIR spectra of these compounds showed stretching vibration in 2113cm⁻¹ and 2135cm⁻¹ for (N≡N). ¹HNMR via solvent (DMSO-d 6) for compound [II]_a display: singlet signals at δ10.14ppm for two protons of N-H groups, signals appear at δ 6.58-7.96 ¹HNMR via

solvent (DMSO-d 6) for compound [II]_b display: a singlet signals at δ9.24ppm for two protons of N-H groups, signals appear at δ 6.56-7.76. ppm for four H-aromatic and a signal at δ 4.03 ppm for 4H of 2(CH₂). Compounds [IV]_a and [IV]_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 carboxyl groups 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 benzamidazole compounds [V]_{a,b} formation from reaction compound [III]_{a,b} with 1,2-phenylenediamine in DMF (as a catalyst). FTIR display absence bands carboxylic acid COO and OH at 1743cm⁻¹ and 3432cm⁻¹ and showed stretching bands at 1498 for (C=N). The compounds [IV]_a and [IV]_b with thionyl chloride in DMF product acid chloride compounds [VI]_{a,b}. The FTIR display absence bands (carboxyl group). Finally compounds 4-carboxy amid [VII-X]_{a,b} product from reaction compounds [IV]_{a,b} with aromatic amines. The characterization FTIR absorption bands for these compounds are listed in Table (2).

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

COMP	ν N-H	ν C-H arom	ν C-H aliph	ν C=O	ν C=C arom
[VII] _a	3265	3089	2915-2855	1642	1578
[VII] _b	3298	3101	2912-2860	1630	1589
[VIII] _a	3294	3092	2963-2898	1633	1604
[VIII] _b	3301	3106	2952-2875	1645	1600
[IX] _a	3311	3087	2957-2896	1639	1607
[IX] _b	3265	3065	2252-2877	1635	1590
[X] _a	3294	3078	2933-2867	1643	1611
[X] _b	3289	3069	2874-2232	1649	1593

Mesophases Behavior

The mesophases and their temperatures were study by (POM) also by differential scanning calorimetry (DSC) The compound [V] showed smectec phase texture (SmA) under polarizing optical microscopy on heating only

as Fig. 1. While the DSC thermogram of compound [V] as in Figure (2), from DSC of this compound the ΔH = -0.524 K J/g. The phase transition temperatures for compounds [V] as below.



In this study, the benaimidazol compound [V]_a display

SmA this is approves with another study [17].

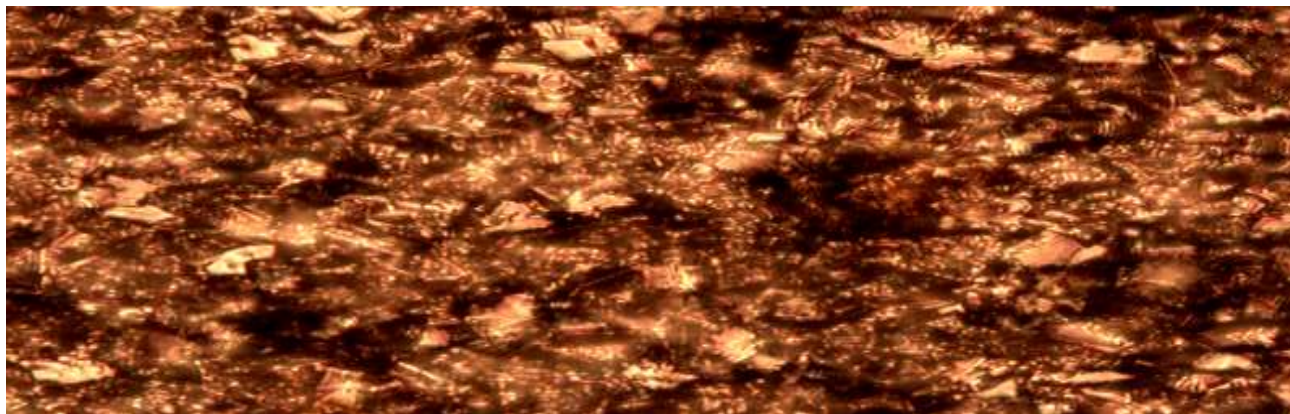
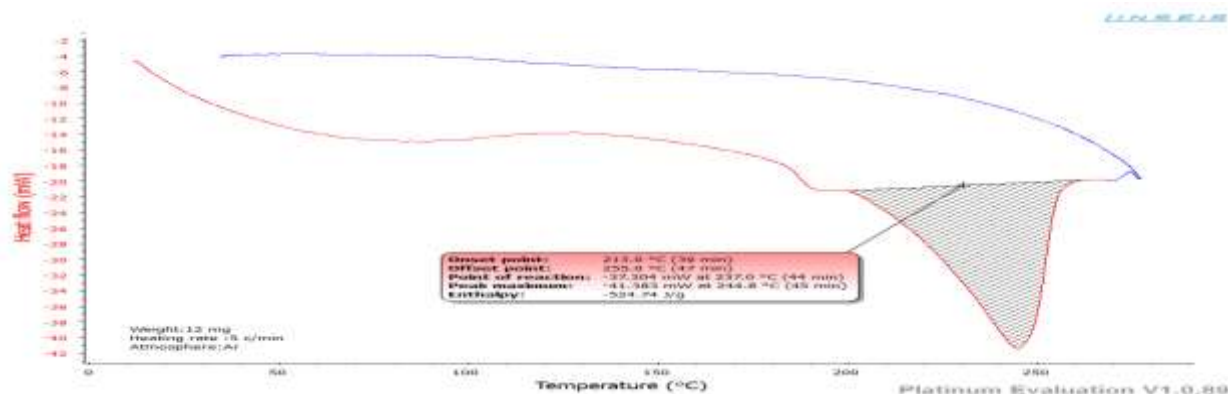
Figure1: Cross polarizing optical textures of SmA of compound [V]_a

Figure 2: DSC thermogram of compound [V]

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