Synthesis and Study the Mesomorphic Behaviour of New N- acetyl and Their Diazetine: Mono and Twin

Thaer S. Ghali
Jumbad H. Tomma
Dept. of Chemistry/College of Education for Pure Science (Ibn Al-Haitham)/
University of Baghdad
Thaer1881@gmail.com
jumbadtomma@yahoo.com

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Abstract

Synthesis ,characterization of new mono and twin compounds containing heterocyclic four member ring as, 1,3- diazetine by four steps. The first step; includes preparation of 2- amino thiazole derivatives [I]$_{a-c}$ via ring closure reaction between acetophenone derivatives with thiourea in I_2, while the second step includes condensation reaction between 2-amino thaizole derivatives[I]$_{a-c}$ and p-methoxy benzaldehyde to produce Schiff bases[II]$_{a-c}$. The third step includes neculophilic attach from imine group toacetyl chloride to give N- acetyl cross bonding[III]$_{a-c}$.Finally ; the fourth step is completed by the reaction of N- acetyl derivatives with sodium azide (NaN_3) to yield new 1,3-diazetines. The synthesized compounds were characterized byNMR and IR spectroscopy. The study of liquid crystalline behaviour was carried out using optical polarising microscopy (OPM) and some of them by differential scanning calorimetry (DSC). All compounds were synthesized which showed liquid crystalline properties on heating.

Keywords: Thiazoles, heterocyclic liquid crystal, N- acetyl derivatives, diazotizes.

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Introduction

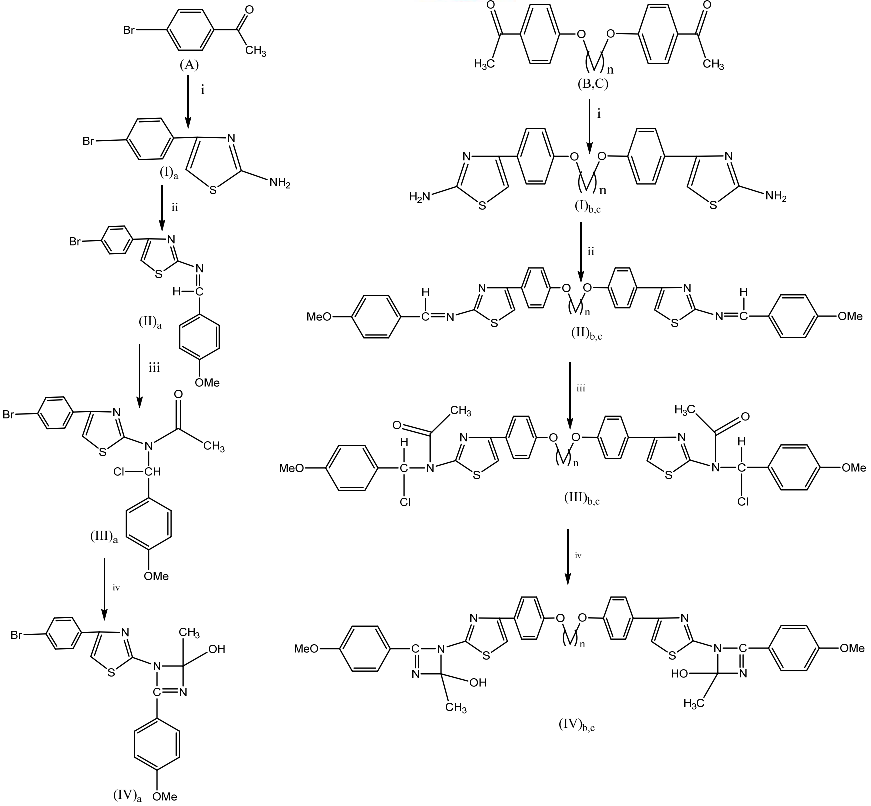
The chemistry of heterocyclic is one of the most complicated branches of organic chemistry[1].Heterocyclic compounds have a wide applications, but very interested in medicinal chemistry and industrial application area [2]. Thiazole is one member of the heterocyclic compound containing both nitrogen and sulfur atoms as a part of aromatic five membered ring. Many workers were interested in thiazoles liquid crystalline compounds containing imine linkage [3-7] studied a correlation. Murzaet. al., [8] have synthesized new liquid crystalline azomethines containing thiazole ring and studied a correlation between the geometric parameters and liquid crystalline properties. On the other hand, Tomma [9] reported the synthesis and study of the liquid crystalline properties of some N- Acetyl derivatives, the study explains enatiotropic mesomorphic behaviour with high transition temperature of the synthesized compounds. A diazetine is a four membered ring with two nitrogen atoms. According to the nitrogen atompositions, the diazetines are existed in two isomeric forms: 1,2 -diazetine and 1,3-diazetine[10]. A diazetine compounds have played a good role as an intermediate in the synthesis of pharmacological active heterocyclic compounds [11]. The addition of alkyl or aryl isocyanates to double bond of N-alkyl andN-aryl carbodiimides to yield 4-arylimino-1,3-diazetidine-2-one derivatives was mentioned by Ulrich et al. [12]. While Lazim [13] synthesized the diazetine from the addition reaction of sodium azide (NaN_3) to N-acyl group. Mormanna and Brahm synthesized and studied mesomorphic properties of 4- isocyanatophenyl 4-methoxybenzoate and the corresponding diazetidinedione[14]. In addition, by intramolecular cyclization of N-aryl thiourea derivatives, Pansuriya prepared new series of 1,3-diazetines [15]. The literatures survey reveals that no evidence for synthesis and study of the liquid crystalline properties of 1,3- diazetines, therefore we decided synthesis, characterization and study of the liquid crystalline properties of new derivatives for new 1,3- diazetines and their N-acetyl.

Experimental

Chemicals: Chemicals were supplied from Merck, GCC and Aldrich Chemicals Co. and used as received.

Techniques: The FTIR spectra were recorded on a Shimadzu (Ir prestige-21) by using potassium bromide discs,.NMR spectra were carried out by company : Ultra Shield 300 MHz, Bruker, Switzerland, at University of Al-Albayt , Jordan, and were reported in ppm(δ), DMSO was used as a solvent with an internal standard (TMS). Uncorrected melting points were determined on Hot-Stage, Gallen Kamp melting point apparatus,DSC thermographs were carried out on a STA PT-1000 Linseis instrument, Ramp rate : 5 ºC/min on heating and cooling, POM was determined using a microscope model PW-BK 5000 PR equipped with a hot-stage system of HS-400 (KER 3100-08S). Thin layer chromatography (TLC) was carried outusing aluminum sheets.

Synthesis: The new compounds were synthesized according to two routes, scheme (1).



Scheme (1): Reactions and reagents: n= 2,3; (i) I_2, NH_2CSNH_2 ; (ii) 4-methoxy benzydehyde , Ehanol,GAA (iii) CH_3COCl,benzene ; (iv) NaN_3 , DMF.

Synthesis of 1,2-bis [4-oxyacetophenone] ethane[A] and 1,3-bis [4- oxyacetophenone] propane[B]. these compounds were prepared according to the procedure that described by Ayyash et. al [16].

Synthesis of 2-amino 1,3-thiazole[I]$_{a-c}$. These compounds were carried out according to the procedure that described by Karam et al.[17].

Preparation of 4-(4-bromophenyl) -2-amine thiazol[I]$_a$. Yield (90 %); m.p : 164-166 ºC Lit [18].**Synthesis of 4,4'-((ethane-1,2- diylbis(oxy)) bis (4,1-phenylene))bis(2-amine thiazol)[I]$_b$.**.Yield (75%);brown powder ,mp: 220-222 ºC; FT-IR(υ cm^{-1}): (3297,3115, NH_2) ,(3060, CH aromatic), (2951, 2885, CH aliphatic),(1620, C=N), (1600 , C=C),(1249 , C-O) ; ^{1}HNMR (DMSO-d_6),(δ ppm): 7.02-7.93(m,10H,Ar-H),6.93(s,2H,NH_2),4.35(s,4H,OCH_2).**Synthesis of 4,4'-((propane-1,3-diylbis (oxy)) bis-(4,1-phenylene))bis(2-amine thiazol)[I]$_c$.**Yield (78%);brown powder, mp:136-138 ºC ; FT-IR(υ cm^{-1}): (3321,3115 , NH_2),(3060, CH aromatic), (2956, 2856, CH aliphatic),(1636, C=N),(1604 , C=C),(1253 , C-O) ; ^{1}HNMR (DMSO-d_6), δ, ppm: 7.01-7.68 (m,10H,Ar-H), 6.95(s,2H,NH_2), 4.2(q,4H,OCH_2) ,2.2 (hextit, 2H,CH_2) ; ^{13}CNMR(DMSO-d_6),(δppm):184.46,169.303,158.63,127.134,126.49,14,64.328and28.53.**Synthesis of new Schiff bases[II]$_{a-c}$.**Dissolved in 5 mL of absolute ethanol a mixture of appropriate 2-amino-1,3- thaizole(0.001mol) and 4-methoxy benzaldehyde (0.001mol) for synthesized compound [II]$_a$ and (0.002 mol) for synthesized compounds [II]$_{b,c}$ with some drops of glacial acetic acid. The reaction mixture was refluxed for 12 hrs. then cooled to room temperature .The filteration of solid product to give new Schiff bases [II]$_{a-c}$ and recrystallization from ethanol .**Synthesis of N-(4-(4-bromophenyl)thiazol-2-yl)-1-(4-**

methoxyphenyl)methanimine [II]$_a$.Yield (69 %);yellow powder, mp:186-188 ºC ; FT-IR(υ cm^{-1}): (3095, CH aromatic), (2929, 2835, CH aliphatic), (1680, 1610, C=N), (1598, C=C).

Synthesis N,N'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene)) bis (thiazole-4,2-diyl))bis(1-(4- methoxyphenyl) methanimine) [II]$_b$ Yield (76 %);yellow needle crystal ,mp: 228-230 ºC ; FT-IR(υ cm^{-1}): (3066, CH aromatic), (2953, 2835, CH aliphatic), (1676,1635, C=N), (1597 , C=C),(1241 , C-O) ; ^{1}HNMR (DMSO-d_6), (δ ppm) : 9.9(s,2H,CH =N), 6.8- 8.1 (m,18H,Ar-H), 4.3 (s,4H,OCH_2) ; ^{13}CNMR(DMSO-d_6), (δppm): 191.29, 166.516, 162.063,157.93, 131.775, 130.476, 129.277, 128.472, 114.476,114.323,113,66.51and55.66.**Synthesis of N,N'-(((propane-1,3-diylbis(oxy))bis(4,1-phenyl- ene)) bis(thiazole-4,2-diyl))bis(1-(4-methoxyphenyl)methanimine) [II]$_c$** .Yield (68 %);yellow powder mp:143-145 ºC ; FT-IR(υ cm^{-1}):(3097, CH, aromatic (2931, 2835, CH aliphatic), (1656,1640, C=N), (1604 , C=C),(1246 , C-O) ; ^{1}HNMR (DMSO-d_6), (δppm) : 9.85 (s,2H ,CH=N) , 6.7- 8.0 (m,18H,Ar-H), 4.4 (t,4H,OCH_2), 3.9 (s,6H,OCH_3) , 2.0-2.3(m,2H,CH_2) ; ^{13}CNMR(DMSO-d_6), (δppm) : 191.29, 166.516 ,162.063,157.939 ,131.779 , 131.296, 130.426 , 129. 217, 129.048 , 128.316, 115.758, 113, 63.485, 55.117 and 28.457.**Synthesis of N-acetyl derivatives[III]$_{a-c}$.**

To a cooled solution of Schiff bases[II]$_a$ (0.01mol.) in (10 mL.) dry benzene, acetyl chloride (0.785 g ,0.01mol) was added dropwise. The solvent was evaporated after refluxing the reaction mixture for 12 hrs. and the residue was washed with water for many times and recrystalized from DMF\ethanol. The same method was used for synthesized twin n-acyl [III]$_a$, except using twice moles from acetyl chloride (0.02) moles instead of (0.01) moles**.** **Synthesis of N-(4-(4-bromophenyl) thiazol-2-yl)-N-(chloro (4-methoxyphenyl) methyl) acetamide [III]$_a$**. Yield (42 %); yellow green powder mp:208-210 ºC; FT-IR(υ cm^{-1}): (3086, CH aromatic), (2958, 2835, CH aliphatic), (1647, C=O),(1630, C=N), (1595 , C=C),(1253 , C-O), (767, C-Cl).

Synthesis of N,N'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylne))bis (thiazole-4,2-diyl))bis(N-(chloro(4-methoxyphenyl) methyl) acetamide)[III]$_b$. Yield (71 %); brown powder ,mp:148-150 ºC; FT-IR(υ cm^{-1}): (3055, CH aromatic), (2954, 2854, CH aliphatic), (1674, C=O),(1655, C=N), (1597 , C=C),(1253 , C-O), (737, C-Cl) ; ^{1}HNMR (DMSO-d_6), δ, ppm: 7.1-8.0(m,18H,Ar-H) ,6.9 (s,2H,CH-Cl), 4.5 (s,4H,OCH_2) , 3.9 (s,6H,OCH_3),2.5(s,6H,CH_3) . ^{13}CNMR (DMSO-d_6),(δ ppm) : 191.29 , 162.063, 157.939,131.775 ,130.476, 129.277 , 128.472, 114.476 , 114.323, 113, 78.604 ,66.51, 55.66 and26.394. **Synthesis of N,N'-(((propane-1,3-diylbis(oxy))bis(4,1-phenylene)) bis (thiazole-4,2-diyl))bis(N-(chloro(4-methoxyphenyl) methyl) acetamide[III]$_c$** .Yield (93 %); dark orange powder mp:140-142 ºC; FT-IR (υ cm^{-1}): (3064,CH aromatic) , (2929, 2820, CH aliphatic), (1676, C=O), (1645 , C=N),(1598 , C=C), (1254 , C-O), (736, C-Cl) ; ^{1}HNMR(DMSO-d_6), (δppm):6.6 -8.0(m ,18H,Ar-H) , 6.3 (s,2H,CH-Cl), 4.7 (t,4H,OCH_2), 3.9(s,6H,OCH_3), 3.4(2H,CH_2), 2.0(s,6H,CH_3).

Synthesis of 1,3-diazetine derivatives[IV]$_{a-c}$.

Sodium azide(0.65g , 0.01 mol) was added to a stirring solution of N-acyl derivatives (0.01mol) in (10 mL) dimethyl formamide(DMF) to synthesize compound [IV]$_a$ while (1.3g ,0.02 mol) was added for synthesized compounds [IV]$_{b,c}$. After the addition, the mixture was heated for 12 hrs. at (55-60) ºC in water bath with stirring. Afterword cooling the reaction mixture to room temperature and filtered the precipitate, washed with cold water and recrystalized from DMF\ethanol. **Synthesis 1-(4-(4-bromophenyl)thiazol-2-yl)-4-(4-methoxyphenyl)-2-methyl-1,2-dihydro-1,3-diazet-2-ol[IV]$_a$**.Yield (91 %);light green powder,mp: 218-220 ºC ; FT-IR(υ cm^{-1}): (3448, OH), (3047, CH aromatic),(2950, 2835, CH aliphatic) , (1662, 1645, C=N),(1600 , C=C),(1249 , C-O) ; ^{1}HNMR (DMSO-d_6), (δppm):

6.8-7.53, (m,9H,Ar-H) ,5.61(s,1H, OH) , 3.6 (s,3H,OCH_3), 1.25 (s,3H,CH_3) . **Synthesis of 1,1'-(((ethane-1,2-diylbis(oxy))bis(4,1-phenylene)) bis (thiazole-4,2-diyl))bis(4-(4-methoxyphenyl)-2-methyl-1,2-dihydro-1,3-diazet-2-ol)[IV]$_b$** .yield (74 %); brown powder , mp: 143-146 ºC ; FT-IR(υ cm^{-1}): (3414, OH), (3041, CH aromatic), (2929, 2837, CH aliphatic), (1665, 1645, C=N),(1600 , C=C),(1242 , C-O) ; ^{1}HNMR (DMSO-d_6), (δppm) :6.7-7.9 (m,18H,Ar-H) ,5.8(broad s,2H, OH),4.25 (s,4H,OCH_2), 3.85 (s,6H,OCH_3) ,1.25(s,6H,CH_3) . ^{13}CNMR(DMSO-d_6),(δppm) :168.537 , 158.457, 157.810, 135.64, 131.788, 130.767, 129.690 , 128.319, 113.590 , 69.696 , 55.665 and28.965.**Synthesis of 1,1'-(((propane-1,3-diylbis(oxy))bis (4,1-phenylene)) bis(thiazole-4,2-diyl))bis(4-(4-methoxyphenyl)-2-methyl-1,2-dihydro-1,3-diazet-2-ol)[IV]$_c$**.Yield (63%),brown powder ,mp: 228-230 ºC; FT-IR(υ cm^{-1}): (3435, OH) , (3074, CH aromatic), (2927, 2854, CH aliphatic), (1676, 1635, C=N),(1600 , C=C),(1248 , C-O) ; ^{1}HNMR (DMSO-d_6),(δ ppm): 6.7- 8.0 (m,18H,Ar-H) ,5.8(broad s,2H, OH) ,4.1-4.25 (broad s,4H,OCH_2), 3.7 (s,6H,OCH_3),2.05-2.2(m,2H,CH_2), 1.25 (s,6H ,CH_3) ; ^{13}CNMR(DMSO-d_6), (δppm): 168.573, 158.186, 157.918, 130.457, 129.437, 128.769, 126.897, 115.941, 114.183, 64.591, 55.092, 31.25 and 28.968.

Results and Discussion

The routes of synthetic for synthesized mono [I-IV]$_a$ and twin [I-IV]$_{b,c}$ compounds are outlined in Scheme (1). All of the synthesized compounds gave satisfactory analysis for the proposed structures, which were conformed on the basis of their Fourier transform Infrared(FT-IR) and ^{1}H ,^{13}C nuclear magnetic resonance (NMR). The di-ketone compounds A and B were prepared based on the methods mentioned in the reference [16]. The first step in Scheme (1) is the synthesis of compound [I]$_{a-c}$ by the reaction of mixture between [A]or[B]or[C] with iodine and thiourea in fusion according to the

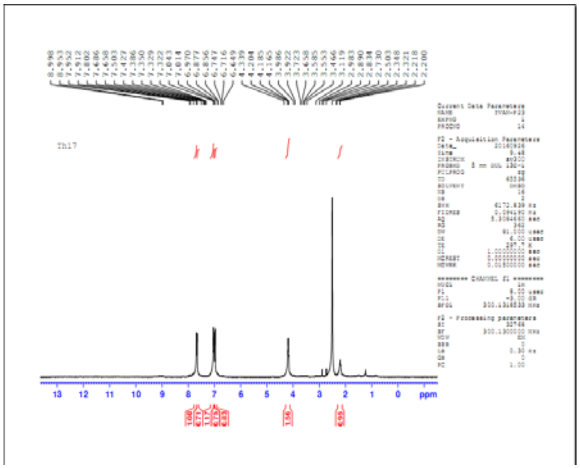


Figure (1):^{1}NMR- spectrumfor compound [I]$_c$

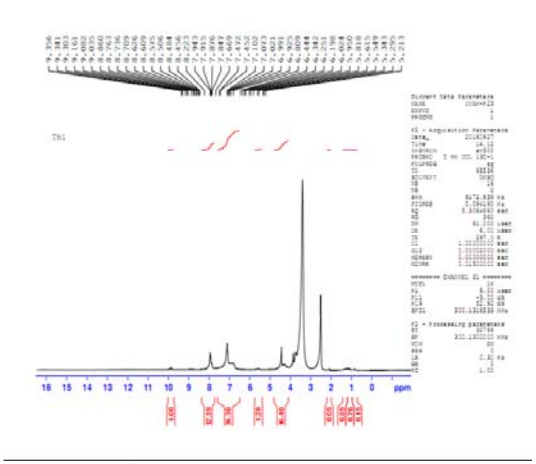


Figure (2):^{1}NMR- Spectrumfor compound [II]$_b$

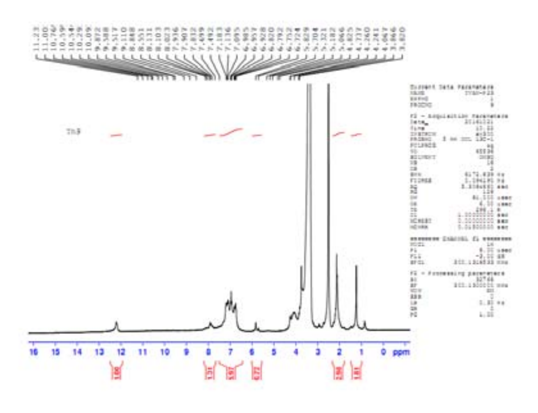


Figure (4):^{1}NMR- spectrumfor compound $[IV]_c$

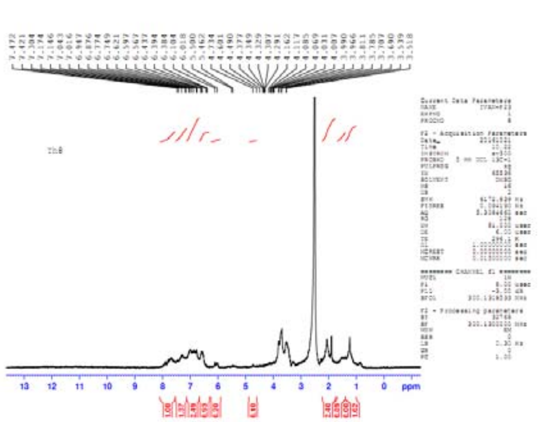


Figure (3):^{1}NMR- spectrumfor compound $[III]_c$

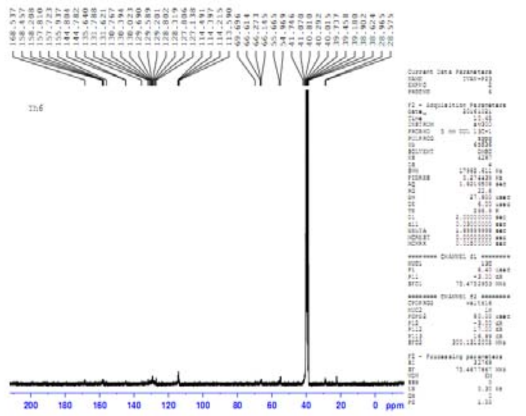


Figure (5):^{13}CNMR-spectrum for compound $[IV]_b$

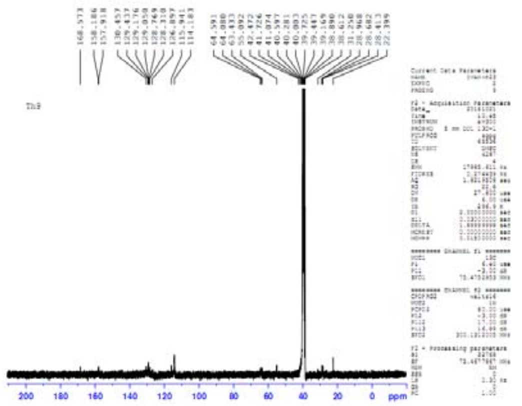


Figure (6):^{13}CNMR-Spectrum for compound $[IV]_c$

procedure in the reference [17] to produce the 2-amino thaizolederivatives. The reaction of compounds$[I]_{a-c}$ with 4- methoxy benzaldehyde leads to the formation of the Schiff base $[II]_{a-c}$ about 68-76% yields. The N- acetyl compound $[III]_{a-c}$ was synthesized by addition reaction of acetyl chloride to Schiff bases $[II]_{a-c}$ in dry benzene about 42-93% yields. The 1,3- diazetine compounds$[IV]_{a-c}$ were synthesized by reaction between N-acetyl compounds $[III]_{a-c}$ with sodium azide (NaN_3) in DMF as a solvent at (55-60)ºC in water bath about 63-91% yields.

Liquid Crystalline Behaviour.

optical polarizing microscopy (OPM) and differential scanning calorimetry (DSC) (of some of them) were used for the study of the mesomorphic properties of all synthesized compounds $[I-IV]_{a-c}$.The chemical structures of mono and twin mesogenic compounds were shown in scheme1. All the synthesized compounds were containing thaizole ring besides to phenyl as a rigid core and strong donating terminal alkoxy groups (OCH_3) see Figure (7), also the mono-mesogenic compounds [I-IV]$_a$ containing Br therefore the later compounds showed different properties than the twin – compounds. The type of transitions and the thermal data of the synthesized compounds were listed in table (1). All compounds[II-IV]$_{a-c}$ exhibited mesomorphic behaviour on heating, while the thaizole compounds [I]$_{a-c}$ did not show any liquid crystalline properties only transition from crystal to isotropic.

Table (1): Type of transition, transition temperatures (T/°C) of compound (I – IV)$_{a-c}$, phase transition enthalpy changes (ΔH.k$_J$. mol^{-1}) and entropies (ΔS.J. mol^{-1}.K^{-1}) of some of them.

Comp. No.	Type of transition	Transition temperature °C	HΔ transition KJ.mol^{-1}	**.SΔ J.mol^{-1}.k^{-1}**
I_a	Cr→ I	166	——	——
I_b	Cr→ I	222	——	——
I_c	Cr→ I	160	——	——
II_a	Cr→ScSc→ N N→I	116.95 203.4 251.2dec.	0.857 0.476 16.53	2.19 0.969 31.54
II_b	Cr→NN→I	139.85 161.1	22.70 1.808	55 4.166
II_c	Cr→NN→I_{dec}	120 300	——	——
III_a	Cr→N N→I	180 210	——	——
III_b	Cr→$N_{discotic}$ N→I	125 150	——	——
III_c	Cr→$N_{discotic}$ $N_{discotic}$→I	113 245.05	2.40 4.66	6.90 8.99
IV_a	Cr→SmC SmC→I	130 230	——	——
IV_b	Cr→$N_{discotic}$ $N_{discotic}$→I	95 >400	——	——
IV_c	Cr→Cr_1 Cr_1→$N_{discotic}$ $N_{discotic}$→N N→ I	85.85 177.75 267.5 300 dec.	4.75 43.16 20.1	13.25 95.77 38.8

Abbreviations: Cr, Cr_1,=crystal phase; N= Nematic phase;Sm= Smectic phase;I=isotropic phase; dec = decomposed

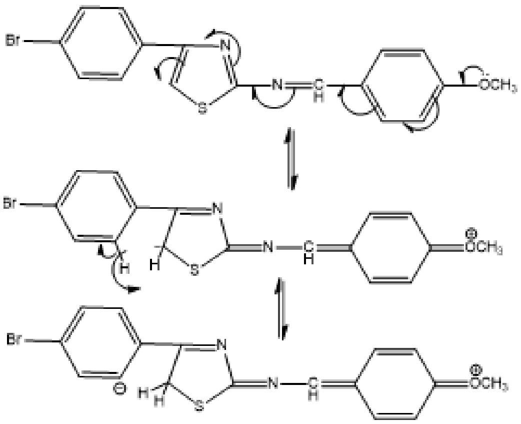
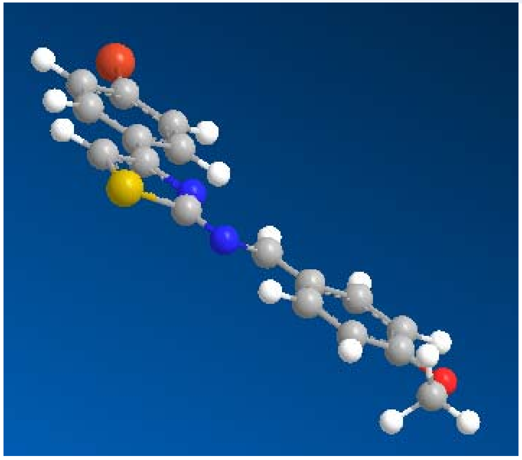


Figure (7): Schematic explains the conjugated bonds in [II]$_a$.

The mesomorphic behavior of mono- mesogenic compounds[II-IV]$_a$ these compounds were similar in terminal group and central core ,but there was a strong difference between them in the linkage group, so in the cohesive forces compound [I]$_a$and did not contain linkage group, the compound [II]$_a$ contains imine linkage C=N (planer sp2 hybrid) that conjugate with thaizole see Fig. 7 ring and phenyl ring led to increase lateral forces and form of both SmC and N mesophases . The Fig. 8 3D structure can explain the linearity of molecule. And figure (9) DSC thermogram of compound [II]a and figure (10) Photomicrographs of[II]a.



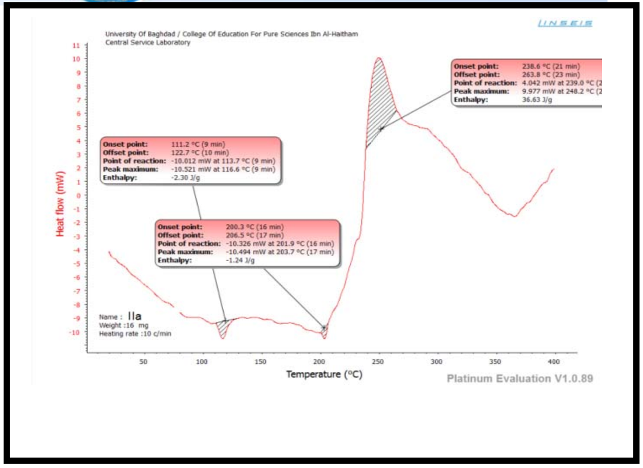
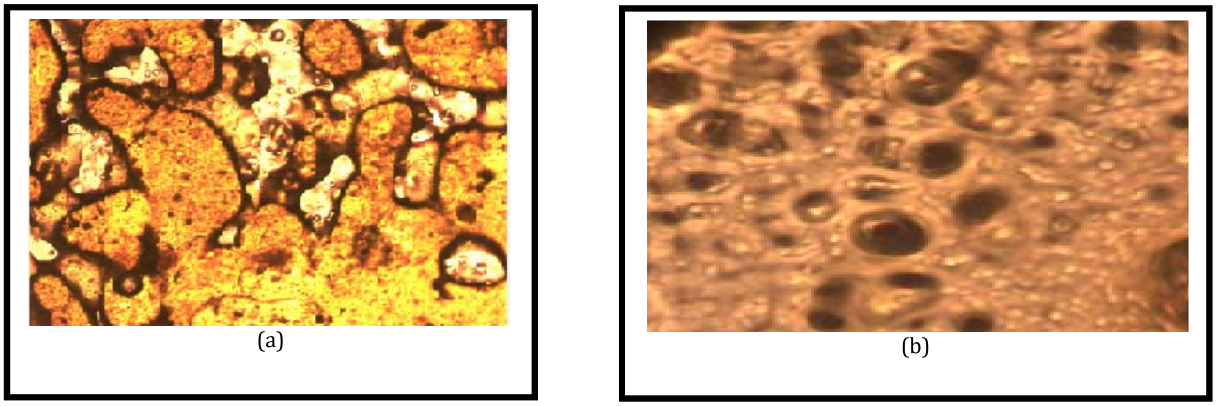


Figure (8): 3D Model of compound [II]a

Figure (9): DSC thermogram of compound [II]$_a$



(a)

(b)

Figure (10): Photomicrographs of (a) Smc texture at 119 ºC on heating for compound [II]$_a$, (b) N(droplets) texture at 206ºC on heating for compound [II]$_a$.

While compound [III]$_a$ contains CH-N (sp^3 hybrid) non planer group and the presence of Cl (Cl-CH-N) causes the random in the mesophase therefore forming only nematic mesophase figure (1) showed 3D model of compound[III]$_a$. 1,3- diazetine compound [IV]$_a$ without linkage group but containing four rings as a central core that causes forming increase in rigidity that reflects smectic phase type SmC with wide mesomorphic temperature ranges than compound [III]$_a$Fig.13(f) showed the smectic phase of[IV]$_a$.

The mesomorphic behavior of twin- mesogenic compounds[II-IV] $_{b,c}$.

The two types of compounds [II-IV]$_b$ and [II-IV]$_c$ have the same chemical structure , the difference between them is methylene spacer $(CH_2)_n$, n=2 in type of compounds [II-IV]$_b$ while n=3 in the second type compound [II-IV]$_c$ this difference may cause change in the geometry of the molecule and change in the terminal and lateral interaction forces ,led to get different type of mesophases and their thermal stability as shown in table (1) .Twin Schiff bases[II]$_{b,C}$ display nematic phase with a wide range of thermal stability figure (13a & 13b) texture of [II]$_{b,c}$, figure (8) DSC thermogram of[II]$_b$ and figure (9) 3D model of [II]$_b$, on the other hand ,the N-acyl compounds [III]$_{b,c}$ showed on heating nematic phase figure (6d & 6e) texture of [III]$_{b,c}$ Finally , the novel 1,3- diazetine compounds [IV]$_{b,c}$ exhibited discotic phase. The presence of 1,3- diazetine ring containing OH group causing deviation in the linearity and geometry of molecule. In addition, the intermolecular hydrogen bonding encourages the discotic shape figure (12) explains this influence, figures (14), (16) and (18) the DSC thermogram of compounds [II]b, [III]C and [IV]C respectively.

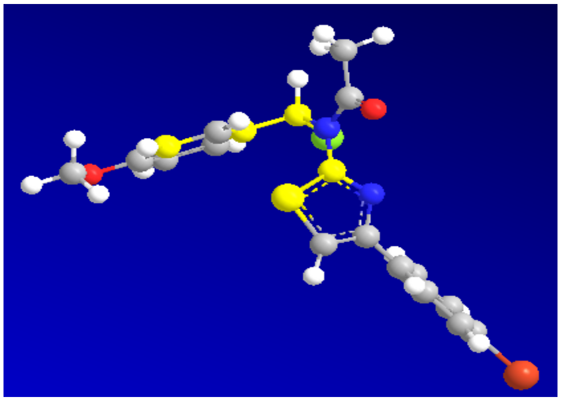


Figure (11): DModel of compound $[III]_a$

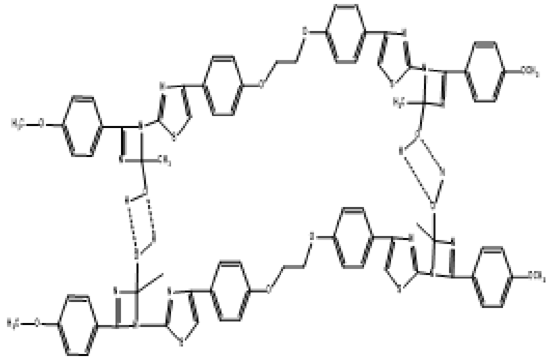
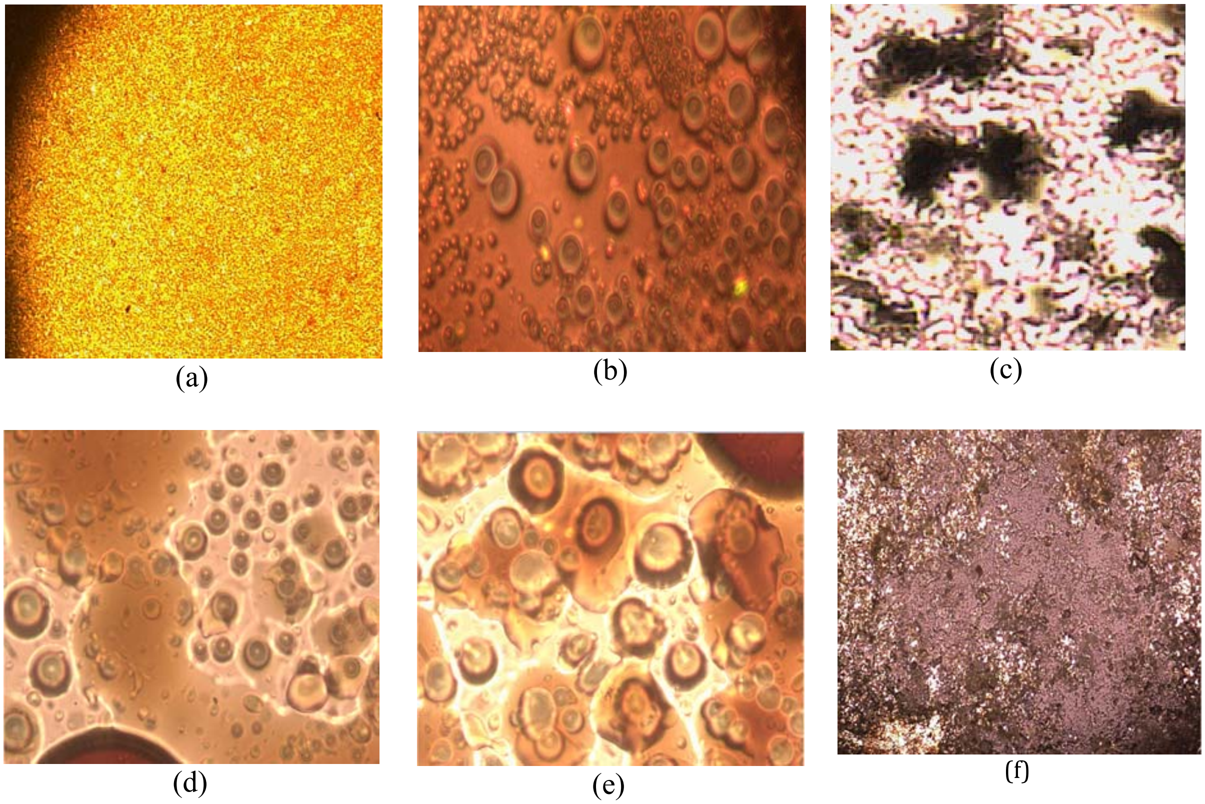


Figure (12): schematic interhydrogen bonding between molecules of compound $[IV]_b$



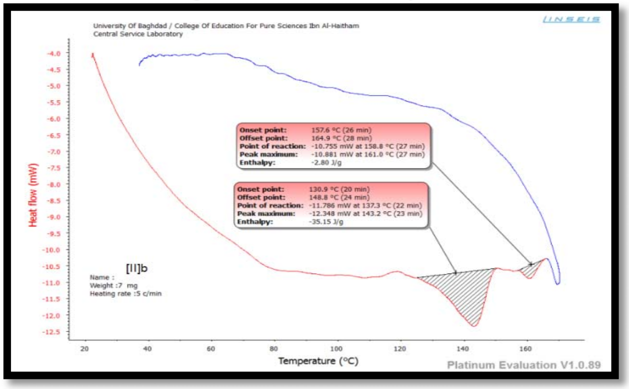
(a) (b) (c)

(d) (e) (f)

Figure(13): Photomicrographs of (a)nematic phase texture at 130 °C on heating for compound $[II]_b$, (b) discotic texture at 240 °C on heating for compound $[II]_c$,(c)N (schlieren)texture at 174-198 °C on heating for compound $[III]_a$, (d) discotic texture at 135°C on heating for compound $[III]_b$, (e) discotic texture at 200 °C on heating for compound $[III]_C$, (f) SmC texture at 135 °C on heating for compound $[IV]_a$.

Conclusions

All the mesogenic compounds were synthesized and characterized containing thaizole and phenyl rings as a rigid core, the study of the liquid crystalline behaviour of these compounds showed LC behaviour with good mesomorphic temperature range. The influence of changing the linkage groups from imine to N-acetyl then to 1,3- Diazetine ring on the mesomorphic proprieties were studied and showed the clear difference between the type of the mesophases and thermal stability of transition phases also the present of the OH groups in compounds[IV]$_{b,c}$ encouraged to appear the discotic phase with a wide range thermal stability.



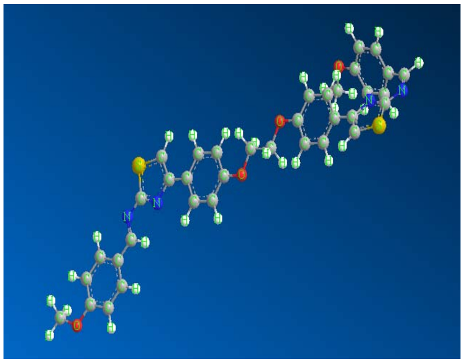


Figure (14): DSC thermogram for compound [II]$_b$. **Figure (15):3D model of compound [II] $_b$**

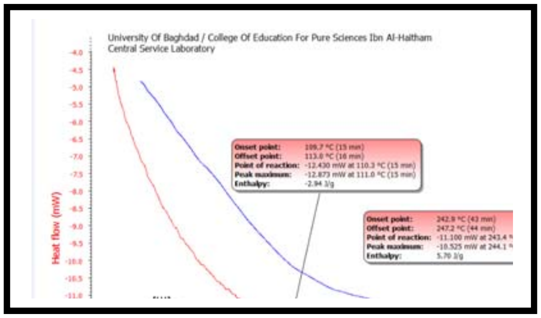
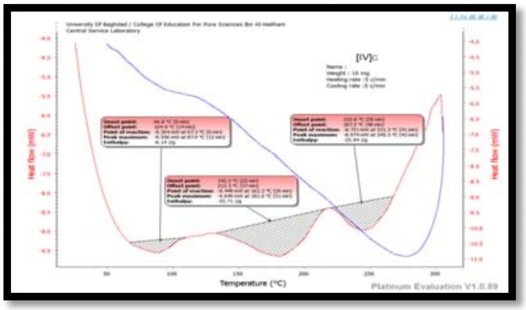


Figure (16) :DSC thermogram for compound [III]$_C$. **Figure (17) :3D model explain hydrogen bonding compound [III]c.**



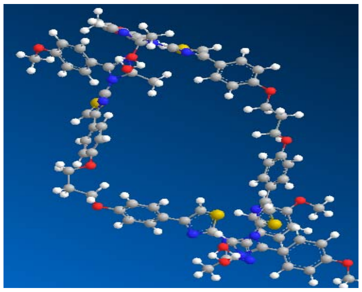


Figure (18): DSC thermogram for compound [IV]$_C$. **Figure (19):3D model explain hydrogen bonding compound [IV]c.**

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