ISSN: 0067-2904

Synthesis, Characterization and Study of The Liquid Crystalline Behavior of Four and Six Heterocyclic Compounds

Nisreen Hussein Karam[1]*, Ivan Hmeed Rouel Tomi[2], Jumbad Hermiz Tomma[1]
[1]Department of Chemistry, College of Education for Pure Science Ibn Al- Haitham, University of Baghdad, Baghdad, Iraq
[2]Department of Chemistry, College of Science, University of Al- Mustansiriyah, Baghdad, Iraq

Abstract

The new compounds synthesized by sequence reactions starting from a reaction of 4-hydroxybenzaldehyde with 1,5-dibromo pentane to produce dialdehyde(I) .Then compound (I) reacted with different aromatic amines to give schiff bases (II-IV),thereafter added acetyl chloride to schiff bases to yield N-acyl derivatives(V-VII).While1,3-diazetine derivatives(VIII-X) were synthesized from the reaction of N-acyl derivatives with sodium azide.The reaction of thiourea with N-acyl compounds led to formation of thiourea derivatives (XI-XIII).Finally, the pyrimidine compounds (XIV-XVI) were synthesized by ring closure reaction of compounds(XI-XIII) with diethyl malonate.The synthesized compounds were characterized by measurements of melting points,FTIR,^{1}H-NMR and mass spectroscopy for some prepared compounds.The liquid crystalline properties were studied by hot stage polarizing microscopy and differential scanning calorimetry DSC for compound (IX). The compounds(VI), (IX),(XII) and (XV) display enantiotropic nematic mesophase, while other compounds(V),(VII),(VIII),(X),(XI),(XIII),(XIV) and(XVI) did not show any liquid crystalline properties.

Keywords:1,3-diazetine, pyrimidine,heterocyclic liquid crystal.

تحضير ، تشخيص ودراسة السلوك البلوري السائل لمركبات رباعية وسداسية الحلقة غير المتجانسة

نسرين حسين كرم[1]*، ايفان حميد روئيل تومي[2] ،جمبد هرمز توما[1]
[1]قسم الكيمياء، كلية التربية للعلوم الصرفة/ ابن الهيثم، جامعة بغداد، بغداد، العراق
[2]قسم الكيمياء، كلية العلوم، الجامعة المستنصرية، بغداد، العراق

الخلاصة

المركبات الجديدة حضرت بتفاعلات متعاقبة تبدأ بتفاعل 4–هيدروكسي بنزالديهايد مع 5,1 – ثنائي برومو بنتان لينتج ثنائي الالديهايد(I) .بعد ذلك المركب (I) تفاعل مع امينات اروماتية مختلفة ليعطي مركبات قواعد شف (II–IV)،بعد ذلك اضيف كلوريدالاسيتايل الى قواعد شف لينتج مشتقاتN – أسيل (V–VII). بينما مشتقات 3,1 – دايازيتين حضرت من تفاعل مشتقات N– أسيل مع صوديوم ازايد .تفاعل الثايويوريا مع مركبات N– أسيل يؤدي الى تكوين مشتقات الثايويوريا(XI–XIII). اخيرا مركبات البيريميدين (XIV–XVI) حضرت من تفاعل غلق الحلقة لمركبات (XI–XIII) مع ثنائي اثيل مالونيت. المركبات المحضرة شخصت بواسطة قياس درجات الانصهار ، طيف الاشعه تحت الحمراء FTIR و طيف الرنين النووي المغناطيسي ^{1}H–NMR وطيف الكتلة لبعض منها .الخواص البلورية السائلة تم دراستها بواسطة مجهر الضوء المستقطب بمنصة تسخين ومسعر المسح التفاضلي DSC للمركب (IX) . المركبات (VI)، (IX)، (XII) و (XV) أظهرت طور نيماتي انعكاسي بينما المركبات الاخرى(V)،(VII) ، (VIII) ، (XI)،(X) ، (XIII)، (XIV)و(XVI) لم تظهر اي خواص بلورية سائلة.

---

*Email:nisreenhkaram@yahoo.com

Introduction

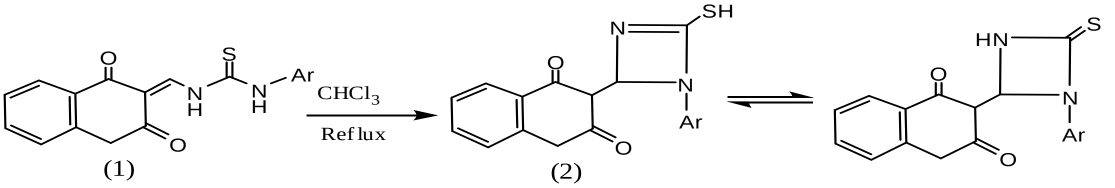
Many workers developed liquid crystal by adding heterocycles to the structures of these compounds, because heterocyclic liquid crystal compounds are used in many applications.

In this study synthesis of new compounds containing two heterocycles 1,3-diazetine and pyrimidine rings. 1,3-diazetine is four- membered heterocycle containing two nitrogen atoms. According to the position of nitrogen atoms the diazetines are existed in two isomeric forms: 1,2-diazetine and 1,3-diazetine[1,2].

Ulrich et al. [3] reported that the addition of alkyl or aryl isocyanates to double bond of N-alkyl and N-aryl carbodiimides to yield 4-arylimino-1,3-diazetidine-2-one derivatives.

Mormanna W. and Brahm M. [4] were synthesized and studied mesomorphic properties of 4-isocyanatophenyl 4-methoxybenzoate and the corresponding diazetidinedione. When present as impurities diazetidinediones decrease the melting point and increase the clearing temperature of the parent isocyanate.

In addition, Pansuriya [5] prepared new series of 1,3-diazetine (2) via intramolecular cyclization of N-aryl thiourea derivatives (1) in chloroform under reflux.

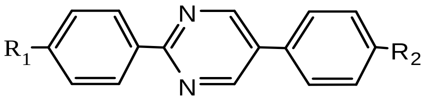


Ar=4-CH_3O-C_6H_4, 3-Cl-C_6H_4, 4-Cl-C_6H_4, 3-O_2N-C_6H_4, 3-Br-C_6H_4 and 2-HO-C_6H_4

While the pyrimidine ring is six-membered heterocycle with two nitrogen atoms in the ring, it has the nitrogen atoms at positions 1 and 3 in the ring[6]. Many workers synthesized liquid crystals compounds with pyrimidine ring as follows:

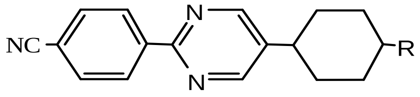
Andrews et al.[7] prepared 2-(4-cyanophenylethyl)-5-alkylpyrimidines and trans-2-(4-(cyano-phenylethyl)-5-alkyl-l,3-dioxanes, which incorporate a dimethylene linking group into phenylpyrimidine and phenyldioxane structures. The pyrimidinyl compounds exhibit only virtual nematic-isotropic transitions and the dioxane compounds have monotropic nematic-isotropic transitions.

Winter et al. [8,9]synthesized two mesogenic compounds 5-phenyl-2-(4-n-butoxy-phenyl)-pyrimidine(3) and 2-phenyl-5-(4-n-pentoxy-phenyl)-pyrimidine(4).Compound (3) display a monotropic nematic phase, whereas compound (4) exhibits a smectic A mesogenic.



(3) when R_1= OC_4H_9 , R_2= H
(4) when R_1=H ,R_2= OC_5H_{11}

Also, Mandal et al.[10,11] and Gupta et al.[12] investigated the crystal structures of three members of the homologous series of 5-(4-n-alkylcyclohexyl)-2-(4-cyanophenyl)-pyrimidines(5).The two lower homologues possess only a nematic phase, while the heptyl compound has a smectic phase in addition to a nematic phase.



R=C_2H_5, C_5H_{11} and C_7H_{15}

(5)

Recently, Kelly et al. [13] studied the position and nature (E/Z) of the double bond were varied systematically and the effect on the liquid crystal transition temperatures of 5-n-alkyl-2-(4-n-alkoxyphenyl)pyrimidines to produce the corresponding alkenyloxy derivatives. The position and nature (E/Z) of the double bond changed the conformation of the alkenyloxy chain substantially. This resulted in higher smectic C and nematic transition temperatures for compounds with a trans-double bond (E) at an even number of carbon atoms. Significantly lower transition temperatures were observed for materials with a cis-double bond (Z) at an odd number of carbon atoms.

Finally, in literature few workers synthesized compounds containing1,3-diazetine with liquid crystals behaviors for this, we synthesized and studied liquid crystalline behaviors of new liquid crystal compounds containing 1,3-diazetine (four member heterocyclic) as while as another type of heterocyclic pyrimidine (six member ring).In addition to investigate the influence on properties of the end groups, different methyl , methoxy and hydroxy are used at the two ends of the molecules.

Experimental

Materials

All starting chemical compounds were obtained from Fluka, Merck, BDH and Aldrich companies.

Instruments

The FTIR spectra were recorded by 600 FTIR spectrometer,(UK).College of Education for Pure Science (Ibn-Al-Haitham)\ Central Service Laboratory , University of Baghdad.

^{1}H-NMR spectra were carried out by company: Bruker , model: ultra-shield 300 MHz , origin : Switzerland and are reported in ppm(δ), DMSO-d_6 was used as a solvent with TMS as an internal standard, measurements were made at Al-albyat University. The mass spectra recorded on Shimadzo model: GCMS QD 1000 EX, (made in Japan) at College of Science, Al-MustansiriyaUniversity. uncorrected melting points were determined by using Hot-Stage, Gallen Kamp melting point apparatus. The transition temperatures and textures of the mesophases were determined by using polarized optical microscope model PW-BK 5000 PR equipped with a hot- stage system of HS-400(KER 3100-08S) and DSC measurements were conducted with STA PT-1000LINSIS.

Synthesize of 4,4'-(pentane-1,5-diylbis(oxy))dibenzaldehyde (I) [14]

In a 100 mL. round bottom flask, 4- hydroxylbenzaldehyde (2.44 g. ,0.025 mol.) was dissolved in 15mL. of N,N-dimethyl formamide (DMF). Anhydrous sodium carbonate (2.65 g., 0.025 mol.) and (0.01 mol.) of 1,5-dibromo pentane were added to the reaction flask. The stirred mixture was heated under reflux for 4hrs. , allowed to cool , then poured into 400 mL. of cold water, cooled at 5°C overnight . The precipitated solid was filtered, washed well with water, dried in air and recrystalized from ethanol to yield 85 %, brown color m.p= 71-73 ^{o}C.

Synthesis of new schiff bases (II-IV)

A mixture of compound (I) (3.12g.,0.01mol.) and different aromatic amines (4-methyl aniline,4-methoxy aniline and 4-hydroxy aniline) (0.02mol.) was dissolved in (5 mL.) of dry benzene with some drops of glacial acetic acid, refluxed for (4 hrs.) and cooled to room temperature.The solid product was filtered to give new schiff bases. The physical properties are listed in Table-1.

Synthesis of N-acyl derivatives (V-VII)[15]

To a stirred cooled solution of schiff bases (II-IV) (0.01mol.) in (10 mL.) dry benzene was added dropwise acetyl chloride (1.4mL.,0.02mol.). The reaction mixture was refluxed for (4 hrs.).The solvent was evaporated and the residue was washed with water for many times. The physical properties are listed in Table-1.

Synthesis of 1, 3-diazetine derivatives (VIII-X) [15]

To a stirring solution of N-acyl derivatives (V-VII) (0.01mol.) in (10 mL.) dimethylformamide, sodium azide (1.3g., 0.02mol.) was added. After the addition, the mixture was heated for (6 hrs.) at (55-60) ^{0}C with stirring, then cooled to room temperature and the precipitate was filtered, washed with cold water. The physical properties of these compounds are given in Table-1.

Synthesis of thiourea derivatives (XI-XIII) [16]

A mixture of N-acyl compound(V-VII) (0.01 mol), thiourea (1.52 g., 0.02 mol.),anhydrous sodium carbonate(2.12 g. , 0.02 mol.) and 20 mL. acetone was refluxed for 4 hrs with stirring. The reaction mixture was cooled and poured onto ice water . After that filtered off to give the product. The physical properties are listed in Table-2.

Synthesis of pyrimidine derivatives (XIV-XVI)[17]

A mixture of thiourea derivatives(XI-XIII)(0.001 mol.) , diethyl malonate (0.002 mol.) and anhydrous sodium carbonate (0.254g., 0.0024 mol.) in dry benzene (10 mL.) was refluxed for 8 hrs. The reaction mixture was cooled and poured onto ice water then extracted with ethyl acetate to yield the product . The Physical properties of these compounds are given in Table -2.

Table 1- Physical properties of the compounds(II-X)

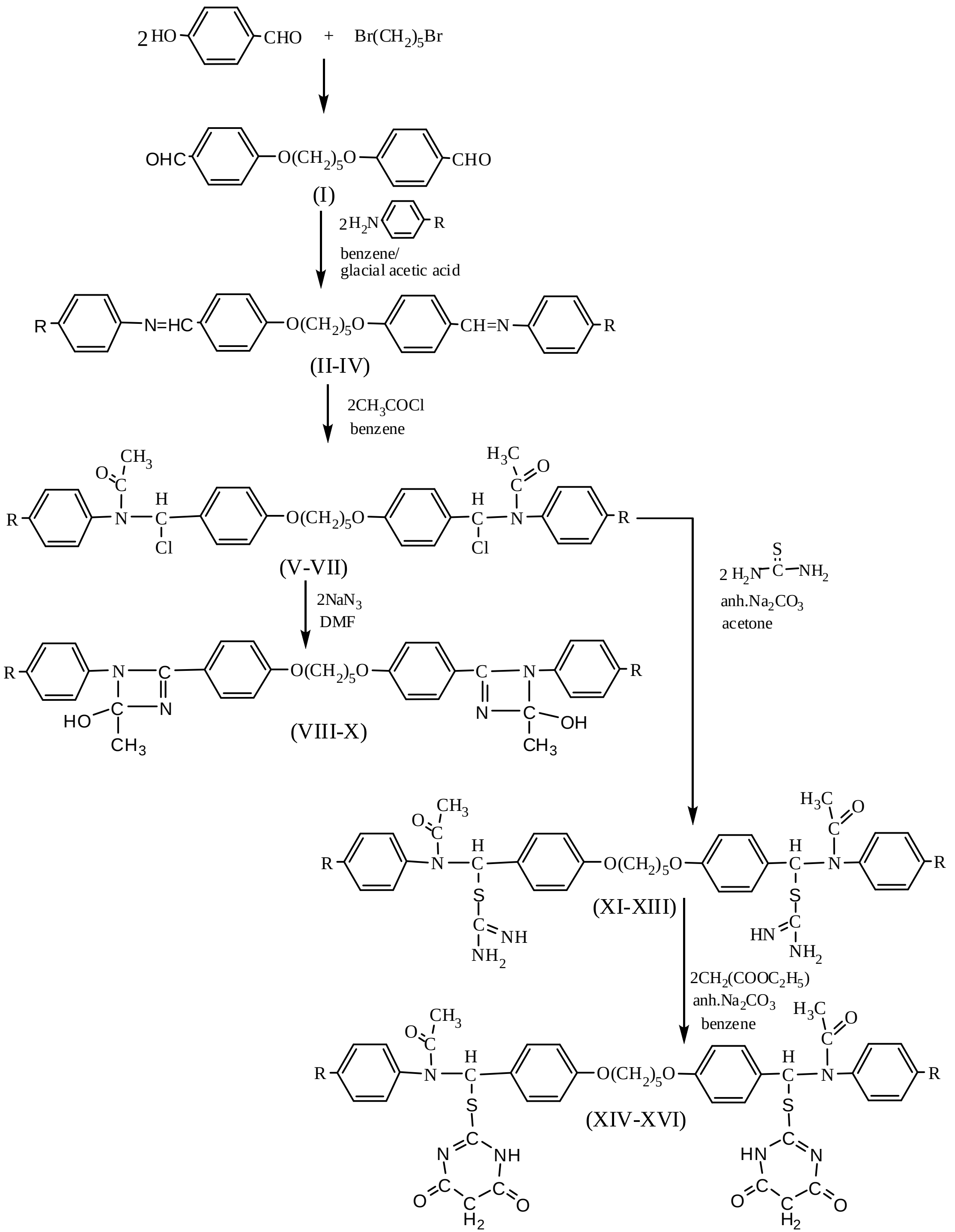
Comp. No.	X	Nomenclature	Molecular formula	Yield %	M. P ^{0}C	Color
II	CH_3	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(4-methylaniline)	$C_{33}H_{34}N_2O_2$	83	137-138	pale brown
III	OCH_3	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(4-methoxyaniline)	$C_{33}H_{34}N_2O_4$	87	179-180	pale brown
IV	OH	4,4'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene)diphenol	$C_{31}H_{30}N_2O_4$	75	203-205	yellow
V	CH_3	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(chloromethylene) bis(N-p-tolylacetamide)	$C_{37}H_{40}Cl_2N_2O_4$	80	165-166	yellow
VI	OCH_3	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(chloromethylene) bis(N-(4-methoxyphenyl)acetamide)	$C_{37}H_{40}Cl_2N_2O_6$	85	210-212	yellow
VII	OH	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(chloromethylene) bis(N-(4-hydroxyphenyl)acetamide)	$C_{35}H_{36}Cl_2N_2O_6$	68	164-166	yellow
VIII	CH_3	4,4'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(2-methyl-1-p-tolyl-1,2-dihydro-1,3-diazet-2-ol)	$C_{37}H_{40}N_4O_4$	65	87-89	brown
IX	OCH_3	4,4'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(1-(4-methoxyphenyl)-2-methyl-1,2-dihydro-1,3-diazet-2-ol)	$C_{37}H_{40}N_4O_6$	78	194-196	off white
X	OH	4,4'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(1-(4-hydroxyphenyl)-2-methyl-1,2-dihydro-1,3-diazet-2-ol)	$C_{35}H_{36}N_4O_6$	61	129-130	brown

Table 2- Physical properties of the compounds(XI-XVI)

Comp. No.	X	Nomenclature	Molecular formula	Yield %	M. P ^{0}C	Color
XI	CH_3	(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis((N-p-tolylacetamido)methylene) dicarbamimidothioate	$C_{39}H_{46}N_6O_4S_2$	74	132-135	off white
XII	OCH_3	(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis((N-(4-methoxyphenyl)acetamido)methylene) dicarbamimidothioate	$C_{39}H_{46}N_6O_6S_2$	80	185-186	off white
XIII	OH	(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis((N-(4-hydroxyphenyl)acetamido)methylene) dicarbamimidothioate	$C_{37}H_{42}N_6O_6S_2$	71	155-156	off white
XIV	CH_3	N-((4,6-dioxo-1,4,5,6-tetrahydropyrimidin-2-ylthio)(4-(5-(4-((4,6-dioxo-1,4,5,6-tetrahydropyrimidin-2-ylthio)(N-(4-methoxyphenyl)acetamido)methyl)phenoxy)pentyloxy)phenyl)methyl)-N-p-tolylacetamide	$C_{45}H_{46}N_6O_8S_2$	68	159-161	white
XV	OCH_3	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis((4,6-dioxo-1,4,5,6-tetrahydropyrimidin-2-ylthio)methylene)bis(N-(4-methoxyphenyl)acetamide)	$C_{45}H_{46}N_6O_{10}S_2$	75	202-204	off white
XVI	OH	N,N'-(4,4'-(pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis((4,6-dioxo-1,4,5,6-tetrahydropyrimidin-2-ylthio)methylene)bis(N-(4-hydroxyphenyl)acetamide)	$C_{43}H_{42}N_6O_{10}S_2$	64	169-170	brown

Results and Discussion

The reactions sequence for synthesis of all new compounds are shown in Scheme-1:



R= CH_3, OCH_3 and OH

Scheme-1

The dialdehyde (I) was prepared by the reaction of two moles of 4-hydroxybenzaldehyde with one mole of 1,5-dibromo pentane, using dry DMF as a solvent in Na_2CO_3 medium . The FTIR spectrum of dialdehydes (I) showed the disappearance of a broad O-H stretching peak with the appearance of C-H aliphatic absorption bands in the region (2943-2843)cm^{-1} and the absorption band of the ether group (C-O-C) at 1249 cm^{-1} besides the good stretching band at 1685 cm^{-1} for aldehydic carbonyl were utilized to confirm the structure of the dialdehydes (I) .

The schiff bases(II-IV) were synthesized by condensation reaction of one mole from dialdehyde (I) with two moles of suitable aromatic amino compounds(4-methyl aniline,4-methoxy aniline and 4-hydroxy aniline) in benzene and some drops of glacial acetic acid .

These schiff bases were characterized by FTIR spectroscopy.

The characteristic absorption bands of new schiff bases are listed in Table -3. FTIR spectra of these compounds (II-IV) showed the disappearance of absorption bands due to NH_2 and C=O stretching band of starting materials together with the appearance of stretching band in the range (1625-1614) cm^{-1} due to C=N(exocyclic) group [18]. N-acyl compounds (V-VII) were synthesized by refluxing two moles of acetyl chloride with one mole of schiff bases(II-IV) in dry benzene. This reaction was started by the attack of the azomethine nitrogen at the carbonyl group of acetyl chloride [19].

These compounds were identified by FTIR and ^{1}H-NMR spectroscopy for compound (VII). The characteristics FTIR absorption bands of N-acyl are given in Table -3.The characteristic FTIR spectra of these compounds showed the disappearance of absorption bands of C═N stretching of schiff bases with appearance of new absorption band in the range (1662-1658) cm^{-1} which is assigned to υ (C=O)acyl, and a new band in the region at (715-752) cm^{-1} can be attributed to υ C-Cl absorption band. The ^{1}H-NMR spectrum of compound (VII) (in DMSO-d_6 as a solvent), Figure-1 showed a multiplet signals in the region δ (1.50-1.98) ppm may be attributed to six protons of(-$CH_2CH_2CH_2$-) group , six protons of $COCH_3$ groups appear as a singlet at δ3.6ppm and a triplet signal at δ 4.25 ppm due to four protons of OCH_2 groups. This spectrum also showed a singlet signal at δ 6.87 ppm that could be attributed to two protons of (CH-Cl) groups, many signals in the region δ (7.10-8.72)ppm that could be attributed to the sixteen aromatic protons.Finally, a signal at δ 10.30 ppm for two protons of OH groups. The 1,3-diazetine derivatives(VIII-X) were obtained by addition reaction of one mole of N-acyl compounds with two moles of sodium azide in dimethylformamide as a solvent at $(55\text{-}60)^0$C temperature. These compounds were identified by FTIR , ^{1}H-NMR and mass spectroscopy for compound (VIII). The FTIR spectra of these compounds (VIII-X) showed the disappearance of absorption bands due to υ C-Cl and υ C═O (amide) with appearance of new absorption stretching bands in the range (1650-1626)cm^{-1} for υ C═N (endocyclic)[15] of diazetine and band in the region (3396-3319) cm^{-1} assigned for O-H bond. The FTIR spectral data for these compounds are given in Table -3. The ^{1}H-NMR spectrum of compound (VIII) (in DMSO-d_6 as a solvent), Figure -2 showed the following signals: a multiplet signals in the region δ (1.59-2.22) ppm due to six protons of (-CH_2CH2CH_2-) group,a signal at δ 2.39 ppm due to six protons of two p-CH_3 groups substituted of benzene rings and and six protons of two CH_3 groups substituted of 1,3-diazetine rings. A signal at 4.10 ppm for four protons of OCH_2 groups. Many signals in the region δ (6.88-7.85) ppm are due to sixteen aromatic protons. Finally, a singlet signal at δ 9.84 ppm can be attributed to two protons of two O-H groups.

Table 3- Characteristics FTIR absorption bands of compounds(I-X)

Comp. No.	**Characteristic bands FTIR spectra(cm^{-1})**				
	υ (O H)	**υ (C- H) aromatic**	**υ (C- H) aliphatic**	**υ (C=C) aromatic**	**other starching bands**
I	-	3049	2943-2843	1600	υ (C=O) 1685
II	-	3018	2943-2864	1600	υ (C=N) 1614 exocyclic
III	-	3062	2931-2864	1606	υ (C=N) 1625 exocyclic
IV	3408	3014	2939-2875	1606	υ (C=N)1616 exocyclic
V	-	3066	2943-2864	1599	υ (C=O) 1662 υ (C-Cl) 752
VI	-	3062	2943-2837	1606	υ (C=O) 1662 υ (C-Cl) 735
VII	3300	3070	2951-2864	1599	υ (C=O) 1658 υ (C-Cl) 715
VIII	3319	3032	2958-2875	1606	υ (C=N) 1, 3-diazetine ring 1650
IX	3388	3010	2931-2833	1600	υ (C=N) 1, 3-diazetine ring 1626
X	3396	3014	2951-2871	1603	υ (C=N) 1, 3-diazetine ring 1630

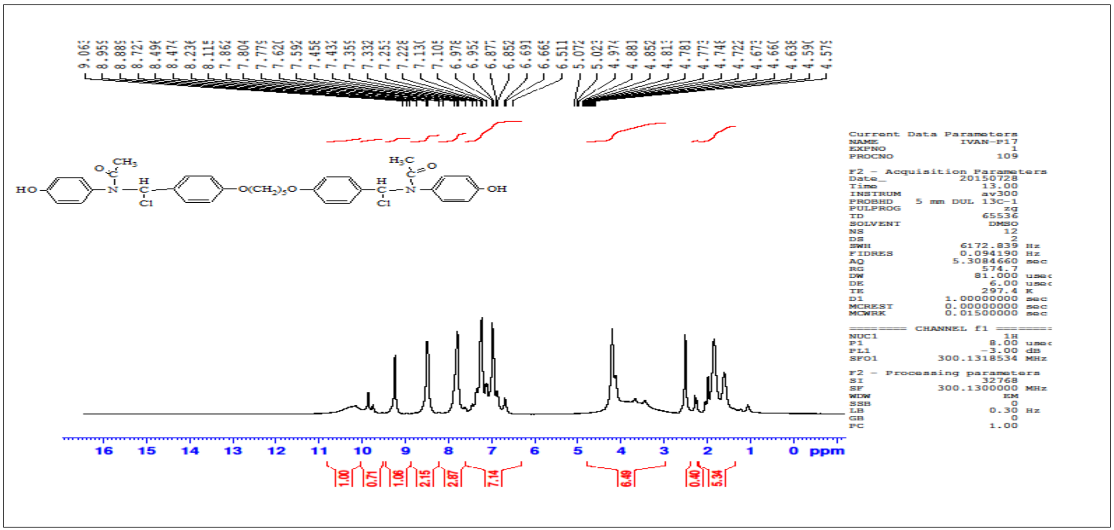


Figure 1- ^{1}H-NMR spectrum of compound (VII)

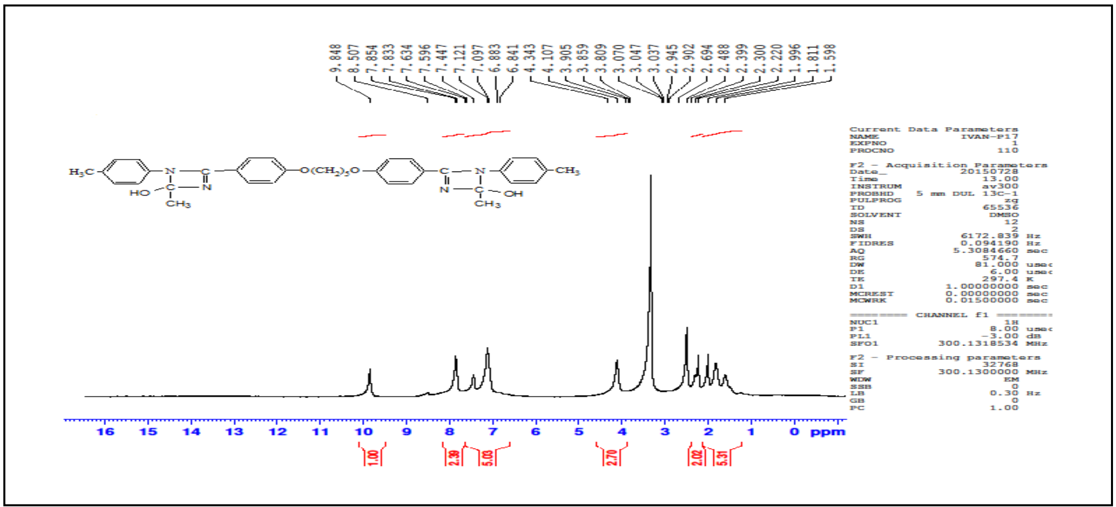


Figure 2- ^{1}H-NMR spectrum of compound (VIII)

The mass spectrum of compound(VIII) , is shown in Figure-3. The peaks at m/z =312, 163, 121, 69 and 41 of characteristic fragmentation of the 1, 3-diazetine ring [20]. While the fragments at m/z = 77, 65 and 51 for the aromaticity of this compound, Scheme -2.

The thiourea derivatives (XI-XIII) were synthesized by reaction of one mole of N-acyl compounds (V-VII) with two moles of thiourea and anhydrous sodium carbonate in acetone .These compounds were characterized by melting points, FTIR and ^{1}H-NMR spectroscopy for compound (XII).

The characteristic absorption bands of new thiourea derivatives are listed in Table-4. FTIR spectra of these compounds (XI-XIII) showed the disappearance of absorption bands due to C-Cl groups of N-acyl compounds with appearance of stretching bands in range at(3417-3100) cm^{-1} and (3150-3100) cm^{-1} assignable to NH_2 and NH groups . The ^{1}H-NMR spectrum of compound (XII) (in DMSO-d_6 as a solvent), Figure-4 showed the following signals: a multiplet signals in the region δ (1.45-1.6) ppm due to six protons of (-$CH_2CH_2CH_2$-) group and six protons of two CH_3 acyl groups at δ 1.8 ppm. A signal at δ3.76 ppm for six protons of two p-OCH_3 groups substituted of benzene rings and four protons of OCH_2 groups at δ 3.88 ppm besides to a signal at δ 4.24 ppm for four protons of two NH_2groups. Also showed signal at δ 4.24 ppm for two protons of (CH-S-) groups. Many signals in the region δ (6.72-7.85) ppm are due to sixteen aromatic protons .

Finally, a signals in the region δ (9.80-10.20) ppm can be attributed to two protons of N-H groups.

While the pyrimidine derivatives (XIV-XVI) were synthesized from reaction of one mole of thiourea derivatives(XI-XIII) with two moles from diethyl malonate and anhydrous sodium carbonate in dry benzene as a solvent . These compounds were characterized by melting points , FTIR and mass spectroscopy for compound(XIV). The FTIR spectra of these compounds (XIV-XVI) showed the disappearance of absorption bands due to υ NH ,NH_2 groups for thiourea derivatives with appearance of new absorption stretching bands in the range (1741-1728) cm^{-1} and (1655-1625)cm^{-1} for υ C═O (pyrimidine ring) and υ C═N (endocyclic) , respectively.

The characteristic absorption bands of new pyrimidine derivatives are listed in Table-4.

The mass spectrum of compound(XIV) , is shown in Figure-5. The peaks at m/z =368, 264, 250, 133, 115,69, and 43 of characteristic fragmentation of the pyrimidine ring[21] . Also the fragments at m/z = 77, 65 and 51 for the aromaticity of compound (XIV), Scheme -3.

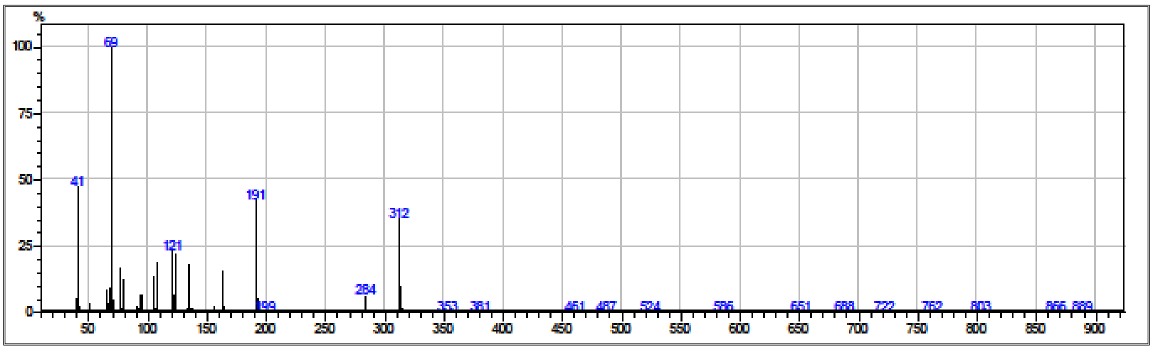
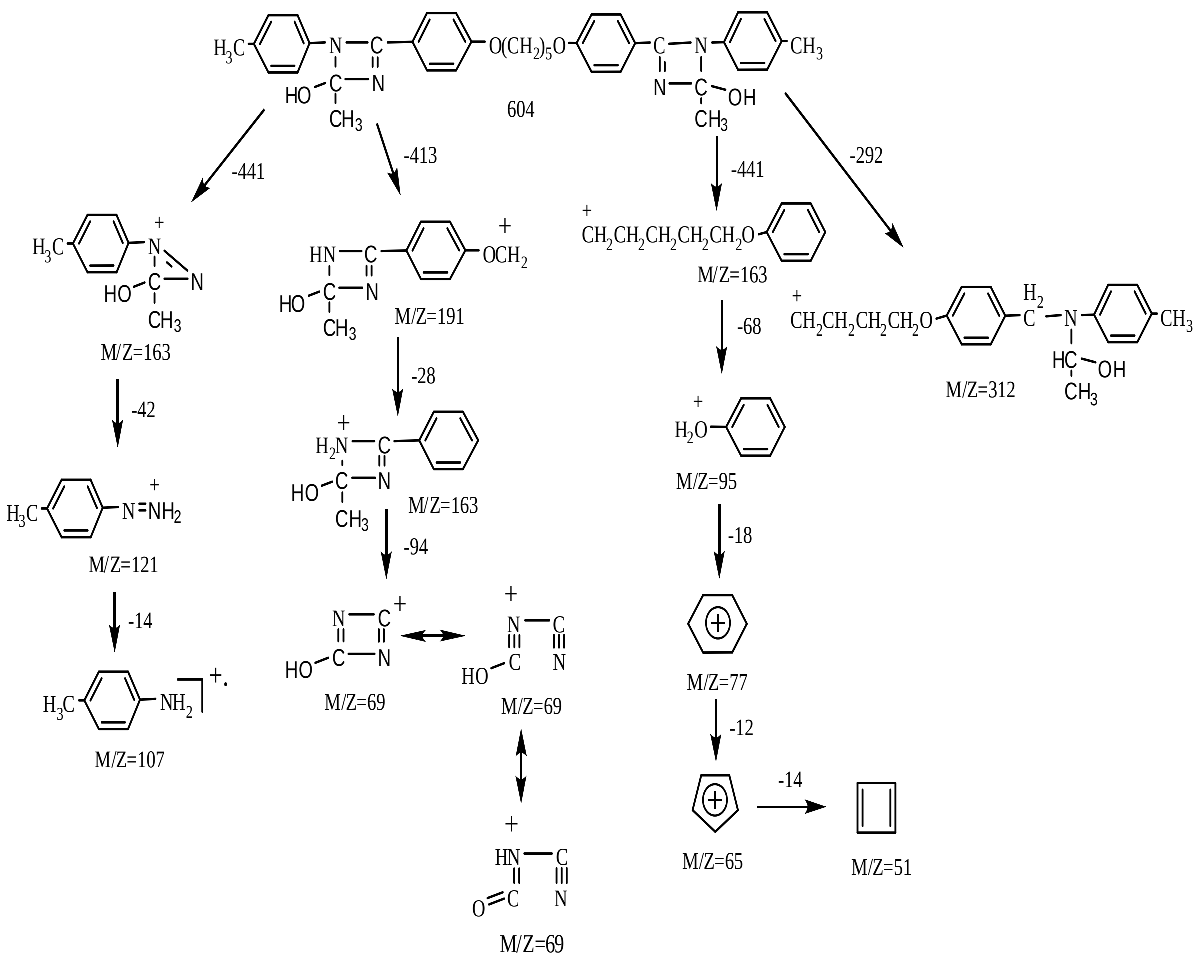


Figure 3- Mass spectrum of compound (VIII)



Scheme 2- Mass fragments of compound (VIII)

Table 4- Characteristics FTIR absorption bands of compounds (XI-XVI)

Comp. No.	**Characteristic bands FTIR spectra(cm^{-1})**							
	υ (N-H)	**υ (C- H) aromatic**	**υ (C- H) aliphatic**	**υ (C=O) pyrimidine ring**	**υ (C=O) acyl**	**υ (C=N) pyrimidine ring**	**υ (C=C) aromatic**	**other starching bands**
XI	3120	3010	2939-2864	-	1689	-	1603	υ(NH_2) sym. asym. 3200-3350
XII	3100	3066	2931-2864	-	1689	-	1606	υ NH_2) sym. asym. 3310-3417
XIII	3150	3066	2947-2868	-	1678	-	1603	υ(NH_2) sym. asym. 3100-3340 υ (O H)3251
XIV	3154	3074	2987-2864	1741	1689	1630	1606	
XV	3120	3010	2985-2943	1728	1670	1655	1590	
XVI	3100	3015	2943-2837	1736	1680	1625	1606	υ (O H) 3421

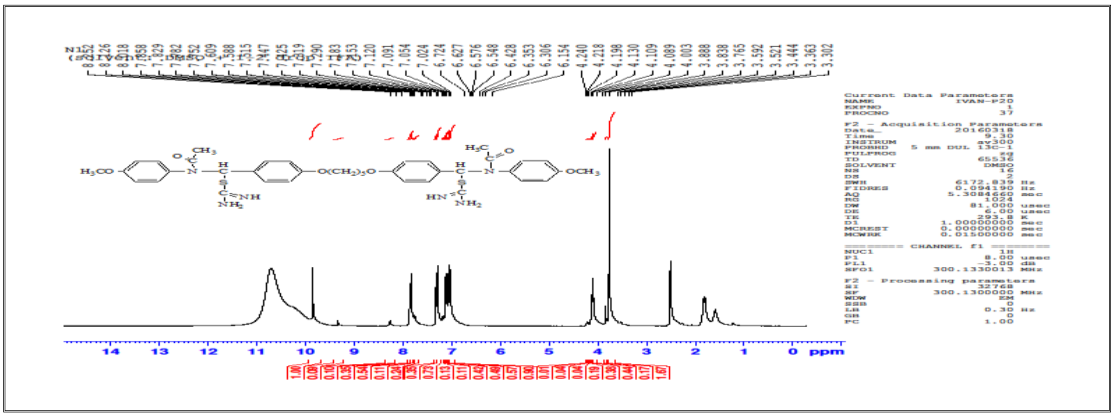


Figure 4- ^{1}H-NMR spectrum of compound (XII)

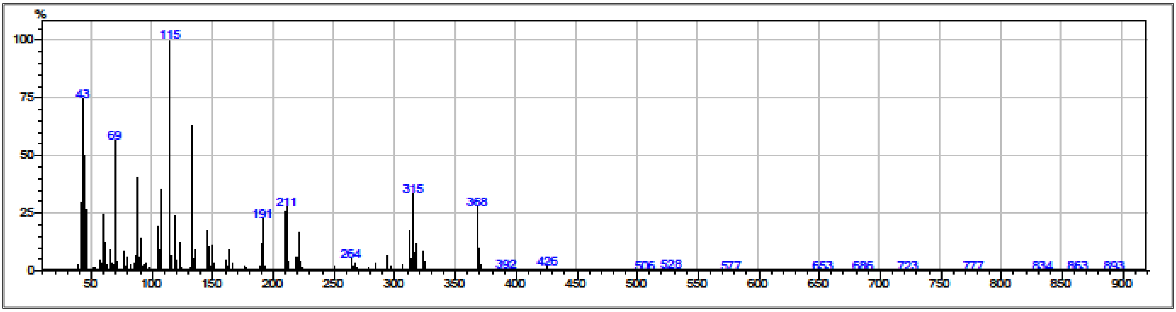
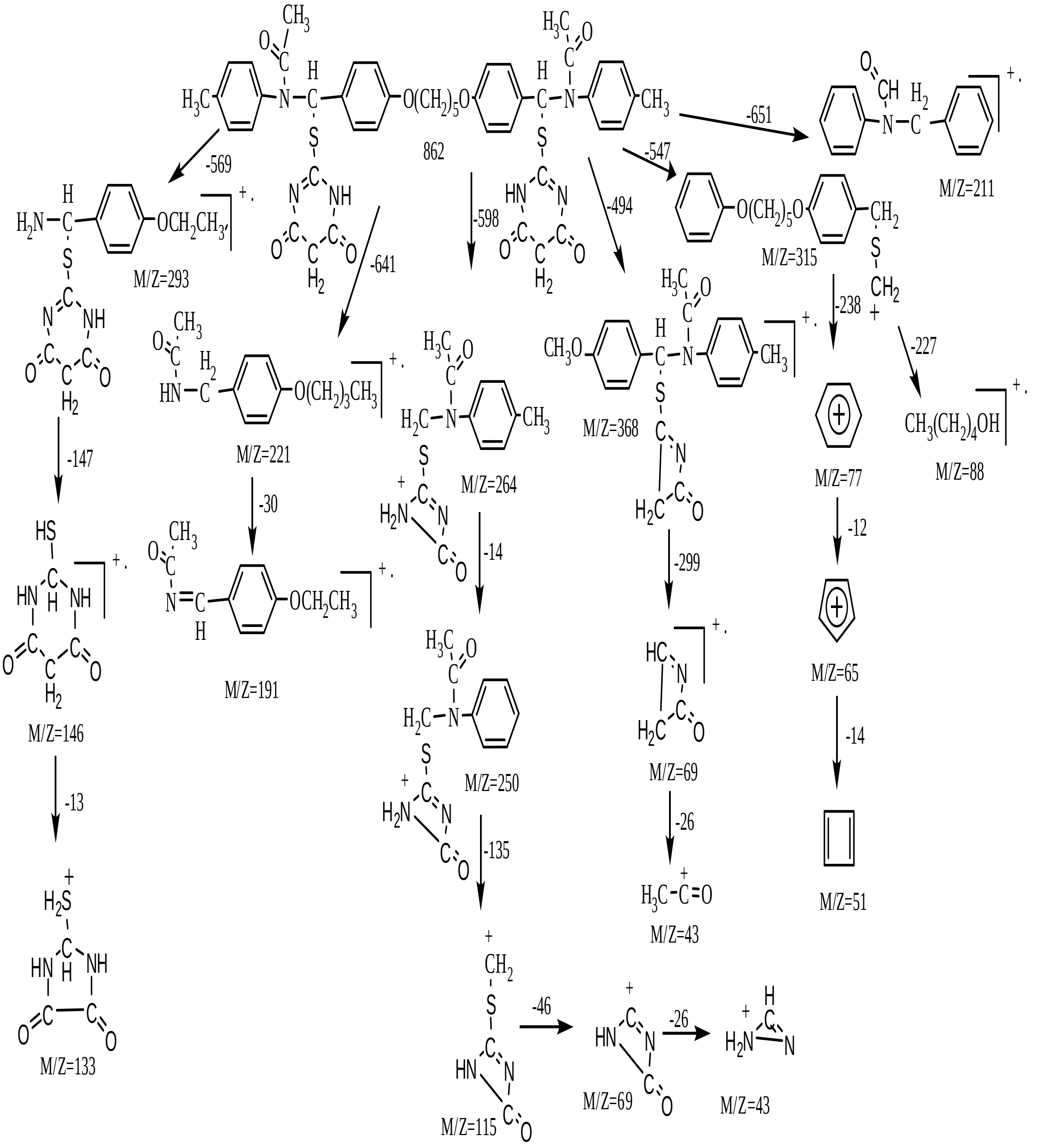


Figure 5- Mass spectrum of compound (XIV)



Scheme 3- Mass fragments of compound (XIV)

Liquid crystals properties

The liquid crystalline properties of all synthesized compounds were investigated by using hot stage polarizing microscopy and differential scanning calorimetry DSC for compound (IX).

The N-acyl compound (VI) showed enantiotropic nematic texture under POM , while the other N-acyl compounds(V) and (VII) do not reveal any liquid crystalline behavior, but simply changes from the crystalline solid state to the isotropic liquid . Also, 1,3-diazetine compound (IX), thiourea compound (XII) and pyrimidin derived from the later compound(XV) display enantiotropic nematic mesophase as Figures-6 and -7 for compounds (IX) and (XII) ,respectively. Figure- 8 showed DSC thermogram for compound (IX).

While, compounds (VIII), (X),(XI), (XIII), (XIV) and (XVI) did not show any mesomorphic behavior.

All the compounds with alkoxy tails form enantiotropic nematic phases but the compounds with alkyl tails do not form liquid crystal this behavior is well known [22] because the alkoxy groups have a higher polarizability than alkyl , 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. Also in this study the behavior of terminal groups (alkoxy , alkyl) on liquid crystals is in agreement with another studies [23]. The phase transition temperatures for compounds (V-XVI) were summarized in Table-5

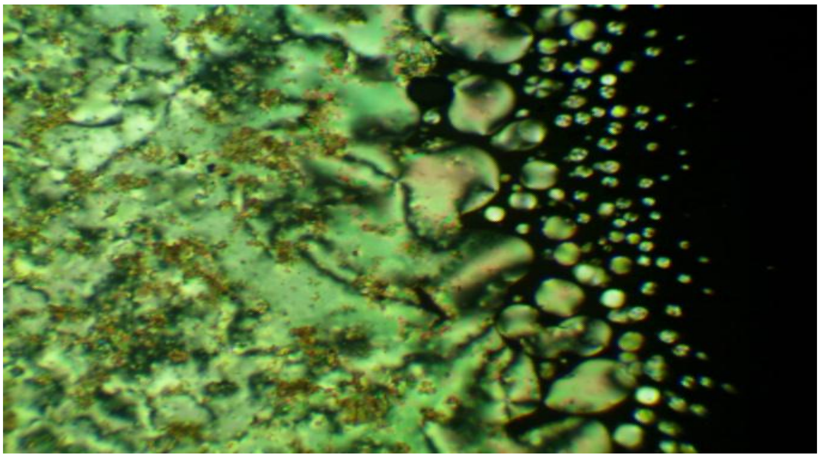


Figure 6- Cross polarizing optical textures of the droplets nematic phase near the isotropic for compound (IX) at 200 °C

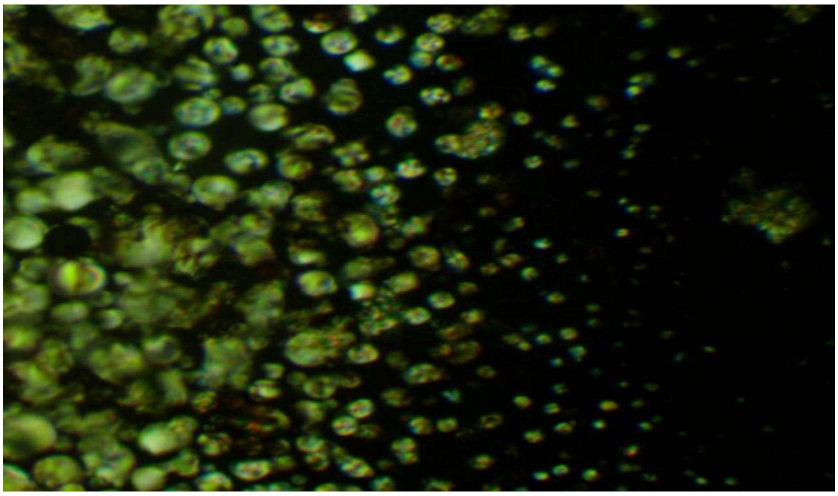


Figure 7- Cross polarizing optical textures of the droplets nematic phase near the isotropic for compound (XII)at 197°C

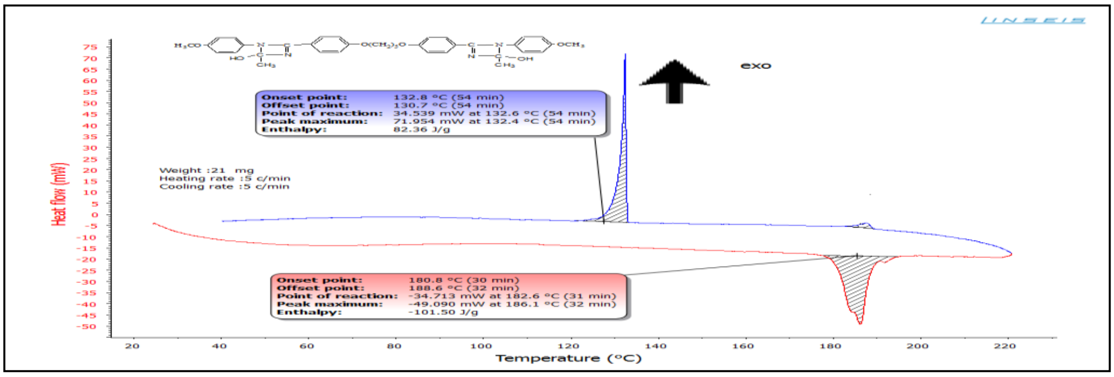


Figure 8- DSC thermogram for compound (IX)

Table 5- Phase transition temperatures (^{o}C) for compounds (V-XVI)

Compound	**Phase transition**
V	$Cr \xrightarrow{170} N$
VI	$Cr \overset{190}{\rightleftharpoons} N \overset{240}{\rightleftharpoons} I$
VII	$Cr \xrightarrow{174} N$
VIII	$Cr \xrightarrow{102} N$
IX	$Cr \underset{132}{\overset{185}{\rightleftharpoons}} N \overset{220}{\rightleftharpoons} I$
X	$Cr \xrightarrow{138} N$
XI	$Cr \xrightarrow{143} N$
XII	$Cr \overset{182}{\rightleftharpoons} N \overset{203}{\rightleftharpoons} I$
XIII	$Cr \xrightarrow{163} N$
XIV	$Cr \xrightarrow{169} N$
XV	$Cr \overset{156}{\rightleftharpoons} N \overset{172}{\rightleftharpoons} I$
XVI	$Cr \xrightarrow{179} N$

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

References

1. Hodgson, D., Stefane, B., Miles, T. and Witherington, J. **2006**. Organolithium-induced alkylative ring opening of aziridines: synthesis of unsaturated amino alcohols and ethers. *Journal of Organic Chemistry*, 71, pp:8510-8523.
2. Lohray, B.B. , Lohray, V.B. and Srivastava, B.K. **2008**. Four-membered heterocycles together with all fused systems containing a four-membered heterocyclic ring. *Molecular Sciences and Chemical Engineering, Journal of Comprehensive Heterocyclic Chemistry*, III(2),pp: 623–687 .
3. Ulrich, H., Richter, R. and Tucker, B. **1987**. [2+2] Cycloaddition reactions of unsymmetrically substituted carbodiimides. *Journal of Heterocyclic Chemistry*, 24(4), pp:1121-1123 .
4. Mormanna, W. and Brahma, M. **1990**. Synthesis and mesomorohic properties of diisocyanatobenzoates. *Journal of Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, Liquid Crystals*,185 (1),pp: 163-169.
5. Pansuriya, A.M. **2009**. Synthesis and pharmacological properties of heterocyclic analogs Ph.D. Thesis. Department of Chemistry, University of Saurashtra, Gujarat, India.
6. Joule, A. J. and Mills, K. **2010**.*Heterocyclic Chemistry* . Fifth Edition. Wiley, Oxford, p:250.
7. Andrews, B. M. , Gray, G. W. and Bradshaw, M. J. **1985**.The preparation and liquid crystal behaviour of pyrimidines and dioxans incorporating a dimethylene linking. *Journal of Molecular Crystals and Liquid Crystals*, 123(1),pp: 257-269.
8. Winter, G ., Hartung, H . and Jaskolski, M . **1987**. Crystal and molecular structure of two isostructural 2,5-diphenyl pyrimidines. *Journal of Molecular Crystals Liquid Crystals*,149, pp:17-27.

9. Winter, G ., Hartung, H ., Brandt, W. and Jaskolski, M . **1987**.Crystal structure and conformational behavior of smectogenic 2-phenyl-5-(4-n-pentoxyphenyl)pyrimidine. *Journal of Molecular Crystals Liquid Crystals*,150b, pp:289-300 .

10. Mandal, P., Paul, S., Stam, C.H. and Schenk, H. **1990**. X-Ray studies of cyanophenyl pyrimidines part II the crystal and molecular structure of 5-(4-ethylcyclohexyl)-2-(4-cyanophenyl)pyrimidine. *Journal of Molecular Crystals Liquid Crystals* , 180(2), pp:369-378.

11. Mandal, P., Majumdar, B., Paul, S., Schenk, H. and Goubitz, K. **1989**. An X-ray study of cyanophenyl pyrimidines. part I-crystal structure of PCCPP. *Journal of Molecular Crystals Liquid Crystals* , 168,(1), pp:135-146 .

12. Gupta, S., Mandal, P., Paul, S. , Wit, De. M. , Goubitz, K. and Schenk, H. **1991**.An X-ray study of cyanophenylpyrimidine part III .crystal structure of 5-(trans-4-heptylcyclohexyl)-2-(4-cyano-phenyl)pyrimidine. *Journal of Molecular Crystals Liquid Crystals* ,195,pp:149-159.

13. Kelly, S. M. , Funfschilling, J. and Villiger, A. **1994**. 2-(4-Alkylphenyl)-5-(alkenyloxy)pyrimidines: Synthesis, liquid crystal transition temperatures and some physical properties. *Journal of Liquid Crystals*, 16(5), pp: 813-829.

14. Griffin, A. C. and Havens, S. J. **1981**. Mesogenic polymers. III. Thermal properties and synthesis of three homologous series of thermotropic liquid crystalline “backbone” polyesters, *Journal of polymer Science, polymer physics*, 19(6), pp:951-969.

15. AL-Aliawi, K. M. L., Tomma, J. H. and Ali, K. F. **2014**.Synthesis and characterization of novel schiff bases, N-acyl and diazetines derived from 3-((5-hydrazinyl-4-phenyl-4H-1,2,4-triazol-3-yl)methyl)-1H-indole.*Advances in Life Science and Technology*,18, pp:77-83.

16. Tomma, J.H.**2010**. Synthesis,characterization and study the liquid crystalline properties of N-acyl, thiourea and imidazole derivatives.*Ibn AL-Haitham Journal for Pure and Applied Science*,23(3),pp:134-151.

17. Al-Abodi, A.J.K., Majed, N., Sahar, A.K. and Al-Bayati, R.I.H.**2012**.Synthesis and characterization of new 1,3-oxazol-5-(4H)-one derivatives. *American Journal of Organic Chemistry*,2(6),pp:143-150.

18. Sharshira, E. and Hamada, N. M. M. **2012**. Synthesis, characterization and antimicrobial activities of some thiazole derivatives . *American Journal of Organic Chemistry*, 2(3),pp: 69-73.

19. Al-Rawi, M., Tomma, J., Mukhlus, A. and Al-Dujaili, A. **2013**. Synthesis and characterization of new schiff bases heterocyclic compounds and their N-acyl, thiourea and imidazole derived from D-erythroascorbic acid . *American Journal of Organic Chemistry* ,3(1),pp: 1-8.

20. AL-Aliawi, K. M. L. **2014**. Synthesis and characterization of new indole derivatives bearing various hetero rings. Ph.D. Thesis. Department of Chemistry ,College of Education for Pure Science, Ibn Al-Haitham, University of Baghdad , Baghdad ,Iraq.

21. Parmar, J.M. and Joshi, N.K. **2012**. Mass spectral fragmentation modes of pyrimidine derivatives. *International Journal Of Chem. Tech. Research*, 4(2), pp: 834-841.

22. Kelker, H., and Hatz, R. **1980**. *Handbook of Liquid Crystals* .Chapter 2. Weinheim: Verlag Chemie, Deerfield Beach, Florida, Basel.

23. Zhang, D. , Zhou, Q.F., Ma, Y.G. , Wang, X. J. , Wan, X.H. and Feng, X.D.**1997**. Synthesis of novel liquid crystal compounds with aromatic amide mesogenic cores. *Liquid Crystals*,23(3), pp:357-363.