



Synthesis ,Characterization and Study of Liquid Crystalline Behavior of New Bent Core Mesogenes Derived From Isophthalic Acid

Fatima A. Abed
Nisreen H. Karam
Jumbad H. Tomma

Dept. of Chemistry/College of Education For Pure Science (Ibn Al- Haitham)/
University of Baghdad

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Abstract

Two series of bent core mesogen containing 1,2,4-triazole ring $[X]_{a-e}$ and $[XI]_{a-e}$ were synthesized by many steps starting from esterification of isophthalic acid with methanol to yield diester compound [I] which was converted to their acid hydrazide [II] and the acid hydrazide reacted with ammonium thiocyanate or phenyl isothiocyanate to yield compounds [III] and [IV] , respectively . Then cyclization by 4% NaOH to yielded 1,2,4 triazole-3- thiol compounds [V] and [VI], respectively, afterword adding hydrazine hydrate to yield compounds [VII] and [VIII] .These compounds condensed with different substituted aldehyde to give new Schiff bases $[X]_{a-e}$ and $[XI]_{a-e}$,respectively.

The synthesized compounds were characterized by melting points , FT-IR and $^1\text{H-NMR}$ spectroscopy (some of them).The liquid crystalline properties were studied by hot stage polarizing microscopy and differential scanning calorimetry DSC for compound $[X]_b$. The compounds $[X]_b$, $[X]_c$ and $[X]_d$ showed mesomorphism properties while the other compounds did not show any mesomorphic behavior.

Keywords: isophthalic acid ,1,2,4-Triazole, , liquid crystal, Schiff bases.

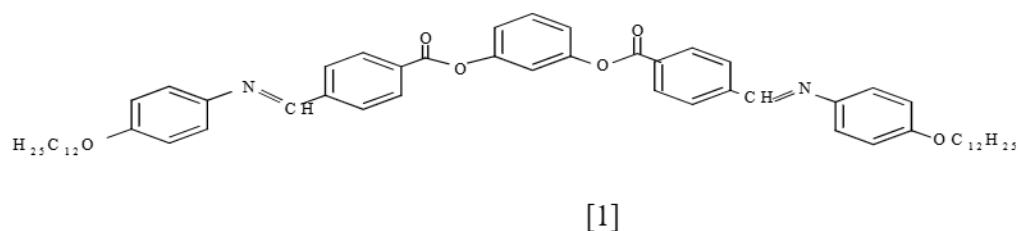
Introduction

Interest in the study of mesomorphic heterocycles has dramatically increased in the recent years due to their wider range of structural templates as well as their optical and photochemical properties [1].

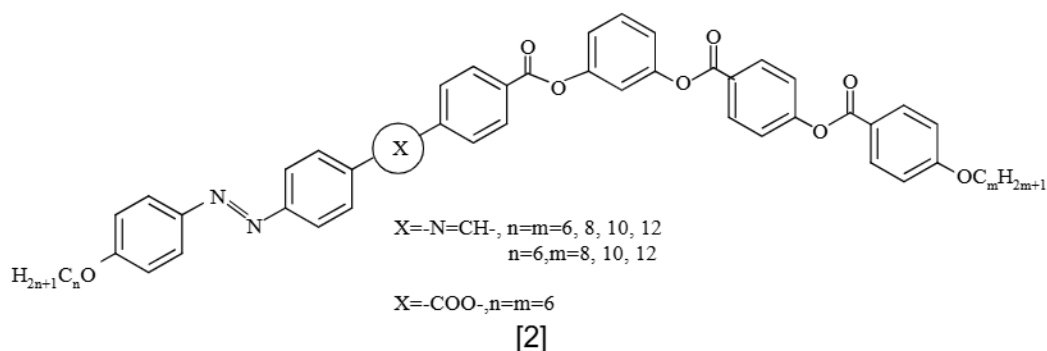
The inclusion of the heteroatom can considerably change the polarity, polarizability and to a certain extent the geometry of a molecule, thus influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens[2]. Examples of liquid crystals with incorporated heterocyclic rings are pyridine [3], oxadiazole[4], benzoxazole[5] and 1,2,4-triazole[6]. In addition when two mesogenic groups linked through a rigid group in such 1,3-position of benzene ring, it means the angle between the two calamitic wings (bending angle) is around 120 degrees[7] this causes bent core mesogen.

In the literature, one may mostly find two aromatic systems used as central ring in bent-shaped compounds: 1,3-disubstituted benzene ring [8,9] and 2,7-disubstituted naphthalene ring[10].

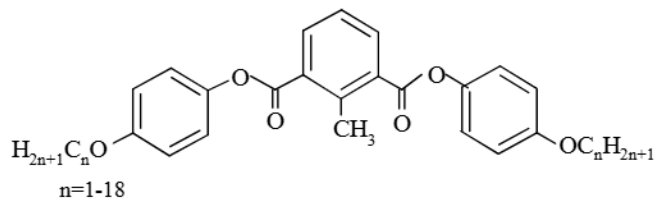
Many workers synthesized bent core mesogen as, J. Thisayukta et al[11] prepared bent core mesogen containing 1,3-benzene ring in a central unit[1].



Also, a homologous series of three- benzene-ring containing bent-cores compounds 1,3-phenylene-bis[4-(alkylcarboxyloxy)benzylideneamino] were synthesized by Huang and Zhai[12]. A new series of bent-core compounds[13] synthesized by using azo linkages with equal as well as unequal terminal alkyl chains[2].



Recently, Weissflog et. al.[14] reported three-ring bent-core bis(4-subst.-phenyl) 2-methyl-iso-phthalates[3] and identified mesophases by their optical textures and X-ray diffraction measurements which exhibiting nematic, SmA and SmC phases.



[3]

The aim of this work is synthesis and study mesomorphic behavior of some new bent core of triazole derivatives.

Experimental

Chemicals

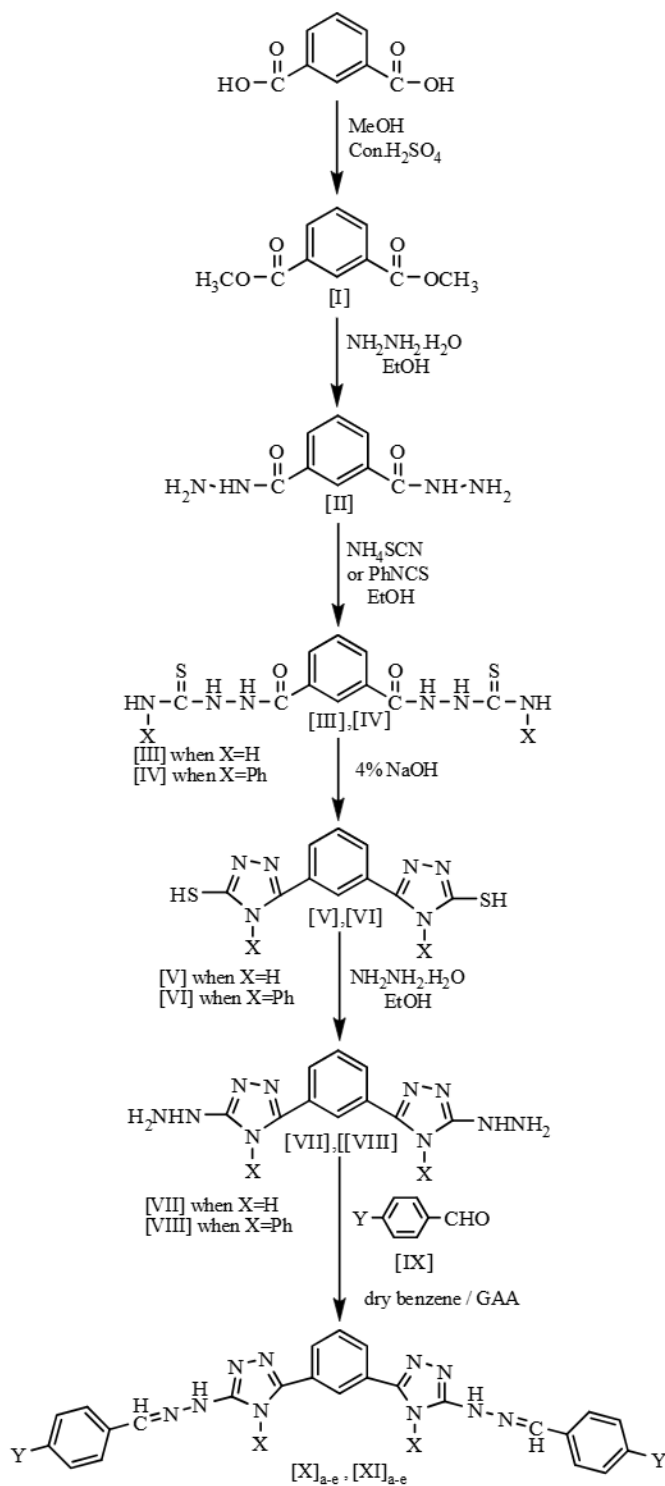
All chemicals were supplied by Fluka, Merck and Aldrich chemicals Co.

Techniques

FT-IR spectra were recorded by 600 FT-IR spectrometer. $^1\text{H-NMR}$ spectra were carried out by company: Bruker, model: ultra-shield 300 MHz, origin: Switzerland and are reported in ppm(δ), DMSO was used as a solvent with TMS as an internal standard, measurements were made at Chemistry Department, Al-Albyat 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 optical microscope model Leica DM2500 Mand DSC measurements were conducted with STA PT-1000LINSIS.

Synthesis

New 1,2,4-triazole compounds are synthesized according to scheme1:



X = H, Ph

Y = NO₂, C_nH_{2n+1}O (n = 1,3,4,8)[X]_{a-e} When X = H[XI]_{a-e} When X = Ph

Scheme (1)

Preparation of dimethylisophthalate[I]

A mixture of Isophthalic acid (40.846 gm , 0.246 mol), in absolute methanol (200 mL) and sulfuric acid (5.4 mL) was refluxed for (6 hrs). After cooling the mixture was washed with sodium bicarbonate solution, then washed with water several times⁽¹⁵⁾, dried and recrystallized from ethanol .The color of precipitate white . yield 71% ; m.p. = 69 °C.

Preparation of Isophthalic acid hydrazide[II]

A mixture of ester compound [I] (0.006 mol) and 80% hydrazine hydrate 3mL in absolute ethanol 5mL was refluxed for (3 hrs). The mixture was cooled at room temperature, solvent was evaporated and the solid formed recrystallized from diethyl ether; the color of precipitate off white ; yield 89%, m.p. = 220 °C.

Synthesis of isophthaylohydrazinecarbothioamide[III]

In absolute ethanol (60 mL) were added acid hydrazide [II] (2.5 gm, 0.013 mol) , ammonium thiocyanate (6gm , 0.078 mol) and HCl (12 mL) refluxed for (22 hrs.) solvent evaporated under reduced pressure. The reaction mixture was added to crushed ice with stirring , precipitated was filtered off , dried and recrystallized from acetone, the color of precipitate yellow , yield 60% , m.p. = 170-173 °C

Synthesis of isophthaylol -N- phenylhydrazinecarbothioamide [IV]

A mixture of acid hydrazide [II] (0.38 g, 0.002 mol) and phenyl-isothiocyanates (0.54 g , 0.004mol) in (20mL) ethanol was refluxed for (4 hrs). The reaction mixture was cooled at room temperature and the solid obtained was filtered, dried and recrystallized from methanol⁽¹⁶⁾; the color of precipitate white , yield 84% m.p. = 195-197 °C

Synthesis of 1,3-phenylene-bis(4H-1,2,4-triazole-3-thiol-5-yl) [V] and 1,3-phenylene-bis(4-phenyl-1,2,4-triazole-3-thiol-5-yl) [VI]

A mixture of carbothioamide derivatives[III] or [IV] (0.01mol) and 20 mL 4% aqueous sodium hydroxide solution was refluxed for (4 hrs). Then resulting solution was allowed to cool to room temperature and acidified with 10% HCl⁽¹⁷⁾. The precipitate formed filtered off, washed with water, and recrystallized from acetone and ethanol, respectively. The compound [V] was yellow color , yield 67% , m.p. = 182-185 °C
The compound [VI] was brown color, yield 78% ,m.p. = 184°C

Synthesis of 1,3-phenylene-bis(5-hydrazinyl-4H-1,2,4-triazole-3-yl) [VII] and 1,3-phenylene-bis(5-hydrazinyl-4-phenyl-1,2,4-triazol-3-yl) [VIII]

To a solution of compounds [V] and [VII] (0.005mol) in 10ml ethanol, 80% hydrazine hydrate (2 mL , 0.04 mol) was added dropwise with stirring and the mixture was then refluxed for (2 days), then the excess of solvent was evaporated and recrystallized these compounds from ethanol and chloroform, respectively. The compound [VII] was off white color, yield 83% , m.p. = 152°C
The compound [VIII] was white color , yield 86%,m.p. = 205 °C

Synthesis of 4-n-alkoxybenzaldehyde [IX]

To a solution of potassium hydroxide (4.87g, 0.087mol) in absolute ethanol 50 ml, 4-hydroxybenzaldehyde (10.61g, 0.087 mol) and n-alkyl bromide (0.13 mol) were added, the mixture was refluxed for 6 hrs., and potassium bromide was precipitated then water 50 ml, diethyl ether 50 ml added. The mixture was extracted, and the organic phase was taken,

washed with 25 ml of water and 25 ml of 10% sodium hydroxide solution, then 25 ml of water. The organic phase was dried over magnesium sulphate, then filtered and evaporated to yield oily 4-alkoxybenzaldehyde, yields (75-80%).

Synthesis of new Schiff bases compounds [X]_{a-e} and [XI]_{ae}

A mixture of compounds [VII] or [VIII] (0.01 mol), a different substituted aldehyde (0.02 mol) in dry benzene (10 mL) and many drops of glacial acetic acid (GAA) was refluxed for (6hrs). The solvent was evaporated under vacuum. The physical data of these Schiff bases are given in Table 1 and 2, respectively.

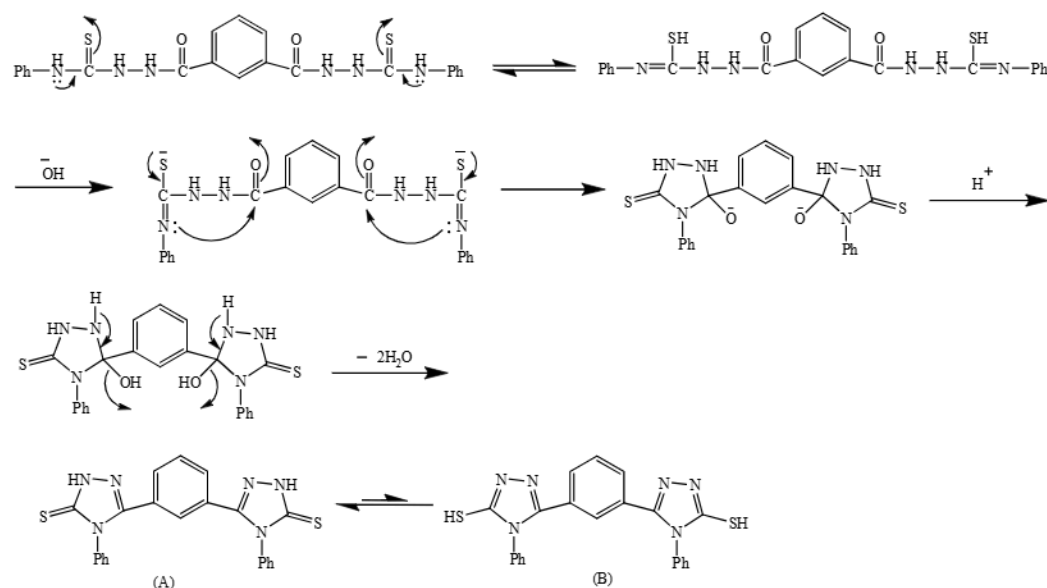
Results and discussion

The ester compound [I] was prepared from reaction isophthalic acid in methanol with Conc. H₂SO₄ (as a catalyst).

The FTIR spectrum for compound [I] 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 1714cm⁻¹ assigned to C=O group of ester moiety.

The condensation of one mole of ester compound [I] with excess of 80% hydrazine hydrate in ethanol produced the acid hydrazide [II]. The compound was characterized by FTIR spectroscopy, the FTIR spectrum for this compound showed stretching vibration to asymmetric and symmetric bands of (N-H, NH₂) groups in the region (3280-3188)cm⁻¹ as well as stretching absorption at 1654cm⁻¹ of ν C=O (amide) and disappearance of absorption stretching band due to ν C=O of ester moiety. The carbthioamide derivatives [III] and [IV] formation from reaction of one mole of acid hydrazide [II] with two mole of ammonium thiocyanate or phenyl isothiocyanate, respectively by nucleophilic addition reaction. The structures of these compounds are identified by FT-IR spectroscopy. FT-IR spectrum of compound [III] showed absorption stretching band at 1232cm⁻¹ that could be assigned to C=S group in addition to new bands which could be attributed to asymmetric and symmetric stretching vibration of NH₂ and NH groups appears between (3277-3116)cm⁻¹, also showed stretching band of ν C=O (amide) group at 1625cm⁻¹, while the FTIR spectrum of compound [IV] appearance of absorption bands in the range (3180-3113) cm⁻¹ assigned for many stretching bands of NH groups, bands at 1672 cm⁻¹ and at 1232 cm⁻¹⁽¹⁸⁾ that could be assigned to ν C=O (amide) and ν C=S groups, respectively.

The cyclization of thiosemicarbazide derivative [III] or [IV] in aqueous sodium hydroxide followed by acidification with hydrochloric acid led to formation of heterocyclic compounds; 1,2,4-triazole-3- thiol derivatives [V] and [VI], respectively. These compounds may exist in two tautomeric forms, thione (A) and thiol (B) according to the position of the mobile hydrogen in the molecule as described in the following mechanism⁽¹⁹⁾ scheme 2.



Scheme (2)

These compounds were identified by FTIR and $^1\text{H-NMR}$ spectroscopy for compound [V].

The FTIR spectra of these compounds [V] and [VI] showed disappearance bands of the ν C=O (amide) groups, which was observed in the starting materials and showed new absorption stretching bands around $\text{cm}^{-1}2694, 2730$ and 1230 , 1253 cm^{-1} that are attributed to the ν SH and ν C=S groups⁽²⁰⁾, respectively. Also, showed stretching band at 1620 cm^{-1} and 1654 cm^{-1} for ν C=N (endocyclic) of 1,2,4-triazole ring, respectively.

The $^1\text{H-NMR}$ spectrum (in DMSO-*d*₆ as a solvent) for compound [V], Figure 1 showed the following signals: a singlet signal at $\delta(14.07)$ ppm for proton of NH triazole ring. Many signals in the region $\delta(7.66-8.72)$ ppm that could be attributed to the aromatic protons and signal appeared at $\delta(1.65)$ ppm for proton of SH group. Finally, the proton at N- of triazole ring (which is tautomerism with SH) appeared at $\delta(7.50)$ ppm[21].

The compounds [VII] and [VIII] were synthesized by nucleophilic substitution reaction of one mole of 1,2,4-triazole-3-thiol compound [V] or [VI] with excess of 80% hydrazine hydrate in absolute ethanol as a solvent. The FT-IR spectra for compounds [VII] and [VIII] showed the disappearance of absorption bands due to (SH) and (C=S) groups of the compounds [V] and [VI] together with appearance of new absorption stretching bands in the region $(3313-3182)$ and $(3301-3155)$ cm^{-1} which is assigned to (NH, NH₂)[22], respectively.

$^1\text{H-NMR}$ spectrum of compound [VIII], (in DMSO-*d*₆ as a solvent), Figure (2) showed: a singlet signal at $\delta 3.58$ ppm for two protons of NH₂ group and many signals in the region $\delta(7.49-7.96)$ ppm that could be attributed to protons of benzene ring. Finally, a singlet signal at $\delta 14.17$ ppm is due to proton of NH group.

The Schiff bases [X]_{a-e} and [XI]_{a-e} were synthesized by condensation reaction of one mole from the compounds [VII] or [VIII] with different aromatic aldehyde in dry benzene.

These Schiff bases were characterized by melting points and FTIR.

The characteristic FTIR spectra of these compounds [X]_{a-e} and [XI]_{a-e}, showed the disappearance of absorption bands due to NH₂ stretching of starting material together with the appearance of stretching band around $(1645-1689)$ and $(1640-1687)$ cm^{-1} assignable to C=N(exocyclic) groups, respectively. The characteristics FTIR absorption bands of new Schiff bases are listed in Table (3) and (4), respectively.

The $^1\text{HNMR}$ spectrum of Schiff bases [XI]_b (in DMSO-*d*₆ as a solvent), Figure (3) showed signal at $\delta 4.07$ ppm due to protons of OCH₃ group, the sharp signal at $\delta 8.43$ may be assigned

to proton of imine (CH=N)group, while a singlet at δ 13.98 ppm can be attributed to proton of NH group. Many signals in the region δ (6.62-7.72) ppm that could be attributed to aromatic protons of phenyl ring.

Liquid crystalline properties

The transition temperatures and mesophase type (texture identity) of all compounds were investigated by using hot-stage polarizing optical microscopy (POM) and by differential scanning calorimetry (DSC) for compound [X]_b.

The phase transition temperatures for compounds of series [X]_{a-e} and [XI]_{a-e} were summarized in Table (5). The compound[X]_b showed nematic texture , while compound [X]_c showed smectic B besides to nematic phase and [X]_d showed dimorphism SmC and N phases under POM besides to, the compound [X]_e didn't showe any mesomorphic behavior . This can be attributed to the chain length of alkoxy terminal group that interferes with liquid crystalline ordering, this could be explained in term of terminal/lateral (t/l) interaction forces ratio. When this ratio is high, compounds tend to give less ordered mesophases (nematic mesophase), while when this ratio is low, the compounds tend to give high order mesohpases (smectic phase)[23]. Figures (4)and (5) showed droplets nematic phase and DSC thermogram for compound [X]_b, respectively.

In this work , it is interesting to compare compounds [X]_{b-d} with compounds [XI]_{b-d} ,these compound have the same central core (1,3-disubstituted benzene ring) and the same alkoxy chain but the difference between the compounds[XI]_{b-d} are the presence of phenyl ring substituted in 4N traizole ring, which will affect on the geometry of a molecule. For this reason, the compounds of series[XI]_{b-d} didn't show any liquid crystalline properties but simply change from crystal to isotropic liquid.

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Table (1): The physical properties for the compounds[X]_{a-e}

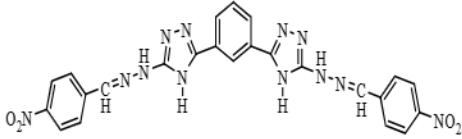
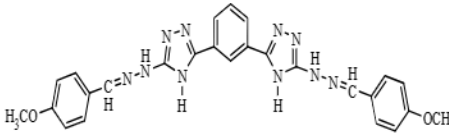
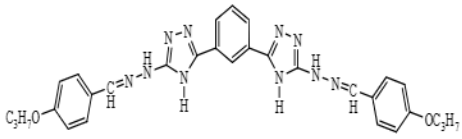
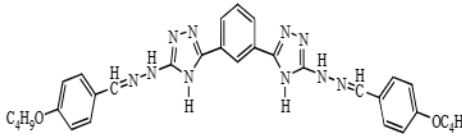
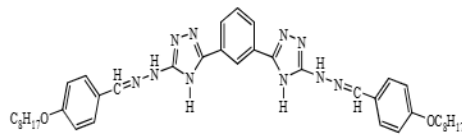
Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P °C	Color
[X] _a	1,3-bis{5-[2-(4-nitrobenzylidene)hydrazinyl]-4H-1,2,4-triazol-3-yl}benzene		C ₂₄ H ₁₈ N ₁₂ O ₄	96	296-298	Yellow
[X] _b	1,3-bis{5-[2-(4-methoxybenzylidene)hydrazinyl]-4H-1,2,4-triazol-3-yl}benzene		C ₂₆ H ₂₃ N ₁₀ O ₂	93	200-201	Yellow
[X] _c	1,3-bis{5-[2-(4-propoxybenzylidene)hydrazinyl]-4H-1,2,4-triazol-3-yl}benzene		C ₃₀ H ₃₂ N ₁₀ O ₂	59	>300	off white
[X] _d	1,3-bis{5-[2-(4-butoxybenzylidene)hydrazinyl]-4H-1,2,4-triazol-3-yl}benzene		C ₃₂ H ₃₆ N ₁₀ O ₂	80	157-159	Yellow
[X] _e	1,3-bis{5-[2-(4-(octyloxy)benzylidene)hydrazinyl]-4H-1,2,4-triazol-3-yl}benzene		C ₄₀ H ₅₂ N ₁₀ O ₂	62	290-292	pal yellow

Table (2): The physical properties for the compounds[XI]_{a-e}

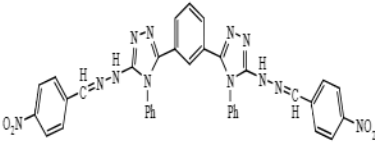
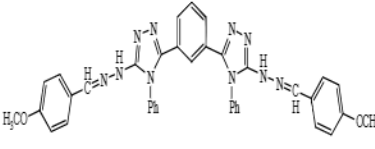
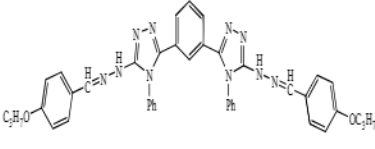
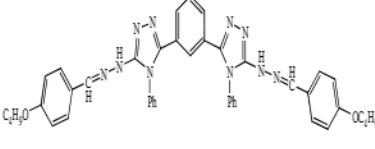
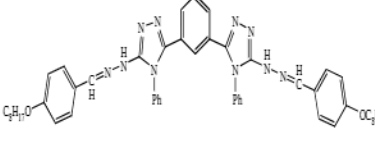
Comp. No.	Nomenclature	Structural formula	Molecular formula	Yield %	M. P °C	Color
[XI] _a	1,3-bis{5-[2-(4-nitrobenzylidene)hydrazinyl]-4-phenyl-1,2,4-triazol-3-yl}benzene		C ₃₆ H ₂₆ N ₁₂ O ₄	59	295- 298	Yellow
[XI] _b	1,3-bis{5-[2-(4-methoxybenzylidene)hydrazinyl]-4-phenyl-1,2,4-triazol-3-yl}benzene		C ₃₈ H ₃₂ N ₁₀ O ₂	90	170- 172	Yellow
[XI] _c	1,3-bis{5-[2-(4-propoxybenzylidene)hydrazinyl]-4-phenyl-1,2,4-triazol-3-yl}benzene		C ₄₂ H ₃₆ N ₁₀ O ₂	59	>300	off white
[XI] _d	1,3-bis{5-[2-(4-butoxybenzylidene)hydrazinyl]-4-phenyl-1,2,4-triazol-3-yl}benzene		C ₄₄ H ₄₄ N ₁₀ O ₂	45	>300	pal brown
[XI] _e	1,3-bis{5-[2-(4-(octyloxy)benzylidene)hydrazinyl]-4-phenyl-1,2,4-triazol-3-yl}benzene		C ₅₂ H ₆₀ N ₁₀ O ₂	45	>300	off white

Table (3) : Characteristics FTIR absorption bands of compounds[X]_{a-e}

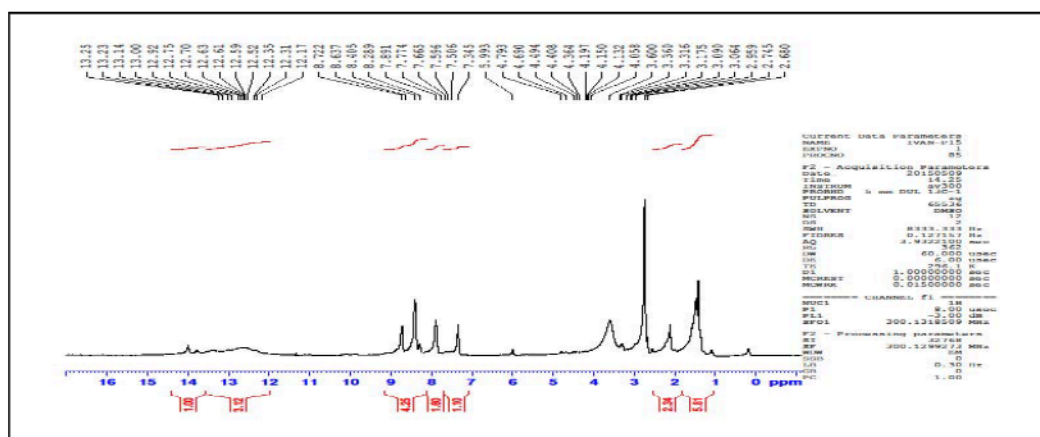
Comp. No.	Characteristic bands FTIR spectra(cm ⁻¹)						
	UNH	U(C-H) aromatic	U(C-H) Aliphatic	U(C=N) exocyclic	U (C=C) Aromatic	U (C-O) ether	Other stretching bands
[X] _a	3294	3012	—	1689	1591	-	P-NO ₂ : 1512,1336
[X] _b	3471	3060	2972-2841	1660	1595	1248	
[X] _c	3210	3022	2964-2879	1676	1595	1249	
[X] _d	3200	3067	2958-2864	1645	1598	1252	
[X] _e	3290	3055	2943-2866	1689	1599	1249	

Table (4): Characteristics FTIR absorption bands of compounds[XI]_{a-e}

Comp. No.	Characteristic bands FTIR spectra(cm ⁻¹)						
	UNH	U(C-H) aromatic	U(C-H) Aliphatic	U(C=N) exocyclic	U (C=C) aromatic	U (C-O) Ether	Other stretching bands
[XI] _a	3110	3066	—	1645	1595	-	P-NO ₂ : 1541,1325
[XI] _b	3350	3064	2908-2810	1687	1591	1240	
[XI] _c	3250	3026	2908-2812	1640	1597	1238	
[XI] _d	3317	3014	2906-2800	1676	1597	1240	
[XI] _e	3290	3061	2916-2815	1687	1593	1240	

Table (5): Phase transition temperatures (°C) of compounds [X]_{a-e} and [XI]_{a-e}

Compound	Phase transition
[X] _a	C $\xrightarrow{303}$ I
[X] _b	C $\xrightleftharpoons[170]{200}$ N $\xrightleftharpoons[200]{170}$ I
[X] _c	Cr $\xrightarrow{230}$ S _B $\xrightarrow{320}$ N $\xrightarrow{345}$ I
[X] _d	Cr $\xrightarrow{135}$ I S _c $\xleftarrow{97}$ N $\xrightarrow{115}$ I
[X] _e	C $\xrightarrow{296}$ I
[XI] _a	C $\xrightarrow{305}$ I
[XI] _b	C $\xrightarrow{180}$ I
[XI] _c	C $\xrightarrow{307}$ I
[XI] _d	C $\xrightarrow{300}$ I
[XI] _e	C $\xrightarrow{309}$ I

Figure (1): ¹H NMR - spectrum of compound [V]

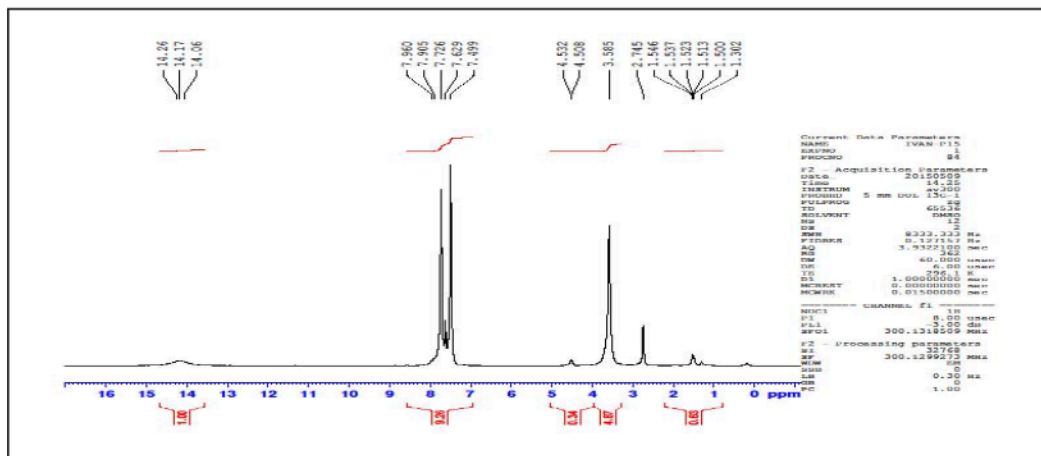


Figure (2): $^1\text{H NMR}$ - spectrum of compound [VIII]

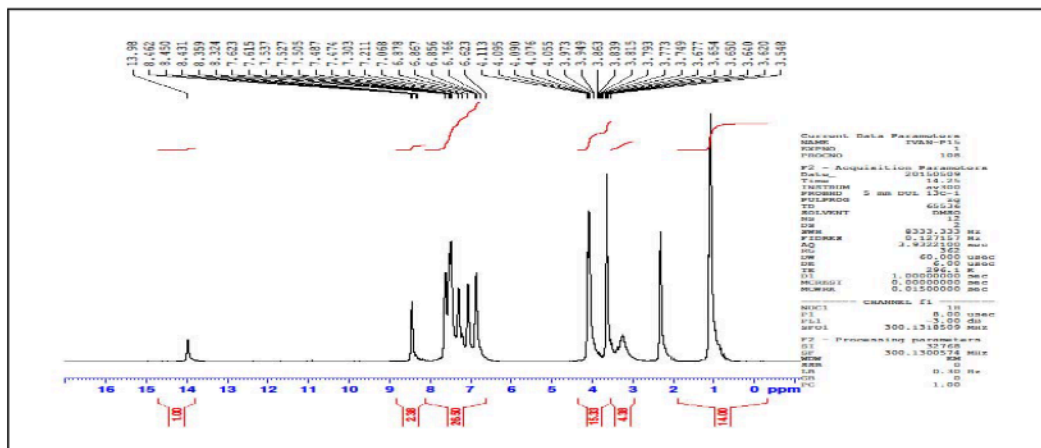


Figure (3): $^1\text{H NMR}$ - spectrum of compound [XI]_b

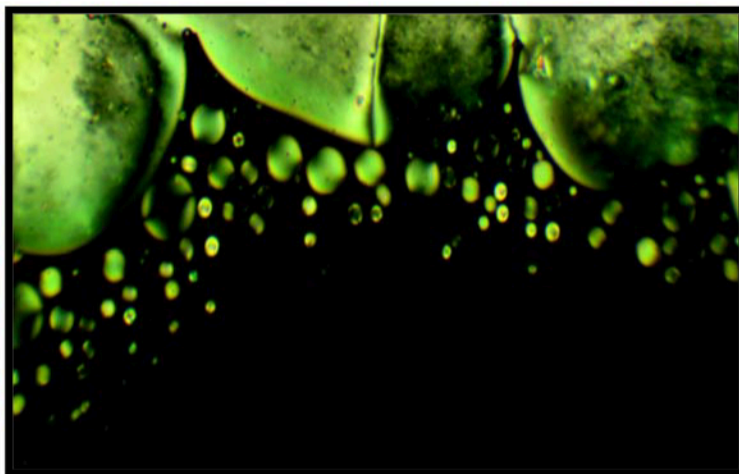


Figure (4): Cross polarizing optical textures of the droplets nematic phase near the isotropic for compound $[X]_b$ at 190 °C

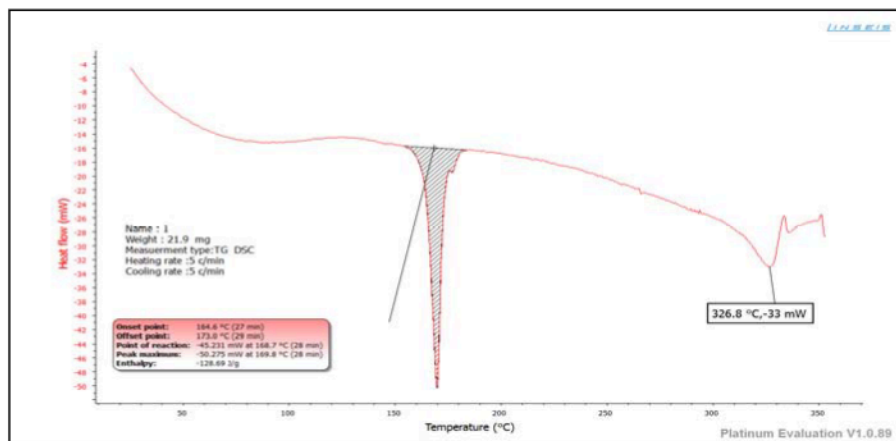


Figure (5): DSC Thermogram of compound $[X]_b$

تحضير و تشخيص ودراسة السلوك البلوري السائل لجزيئات جديدة منحنية المركز مشتقة من حامض الايزوفثاليك

فاطمة أحمد عبد

نسرين حسين كرم

جميد هرمز توما

قسم الكيمياء/كلية التربية للعلوم الصرفة (ابن الهيثم)/جامعة بغداد

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الخلاصة

تم في هذا البحث تحضير سلسلتين منحنية المركز $[X]_{a-e}$ و $[XI]_{a-e}$ وذلك بعدد من الخطوات تبدأ باسترة حامض الايزوفثاليك مع الميثانول لينتج مركب ثنائي الاستر [I] الذي يحول الى حامض الهيدرازيد ومن مفاعلة الاخير مع امونيوم ثايوسينات او فنيل ايزوثايوسينات ينتج المركبين [III] و [IV] على التوالي ومن الغلق الحلقي بواسطة 4% هيدروكسيد الصوديوم نحصل على المركبين 1 و 2 و 4-ترايازول-3-ثايول [V] و [VI] على التوالي بلية اضافة الهيدرازين المائي لينتج المركبين [VII] و [VIII]. ومن تكثيف المركبين الاخيرين مع الديهايدات مختلفة التعويض نحصل على قواعد شف جديدة $[X]_{a-e}$ و $[XI]_{a-e}$ شخصت المركبات المحضرة بواسطة درجات انصهارها، طيف الاشعة تحت الحمراء FT-IR و طيف الرنين النووي المغناطيسي ^1H-NMR لبعض منها. الخواص البلورية السائلة تم دراستها بواسطة مجهر الضوء المستقطب المزود بمنصة تسخين ومسعر المسح التفاضلي DSC للمركب $[X]_b$. اظهرت المركبات $[X]_b$ و $[X]_c$ و $[X]_d$ الخواص البلورية السائلة لكن بقية المركبات لم تظهر اي سلوك بلوري سائل.

الكلمات المفتاحية: حامض الايزوفثاليك, 1 و 2 و 4-ترايازول, البلورات السائلة, قواعد شف.