

Synthesis and Phase Transition Study of New Mesogenes Derived from 1, 4-Phenylenediamine

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Abstract

This work includes the synthesis and characterization of the compound [I] by reaction of 1,4-phenylenediamine with chloroacetic acid, then this compound reacts with methanol in the presence of sulfuric acid to synthesize an ester compound [II]. After that, reaction with hydrazine hydrate synthesizes an acid hydrazide [III], and the later compound reacts with substituted acetophenone [IV]_n to synthesize substituted acetophenone hydrazones [V-XI]. In addition, 4-formylpyrazole derivatives [XII-XVIII] are synthesized via cyclization of substituted acetophenone hydrazones [V-XI] with Vilsmeier-Haack reagent DMF/POCl₃. The compounds are characterized by melting points, FTIR, ¹H-NMR and mass spectroscopy. The mesomorphic behavior is studied by using polarized optical microscopy and differential scanning calorimetry.

Keywords: *Liquid crystals, 4-formylpyrazole, 1, 4-phenylenediamine, Mesomorphic properties.*

Introduction

A number of liquid crystalline compounds containing five-member heterocycles have been synthesized [1, 5]. The LC compounds containing heterocyclic groups have been synthesized due to their potential wide range of multidisciplinary applications such as in molecular devices [6], optical storage and sensors [7, 9]. Thus, interest in mesomorphic heterocyclic compounds has increased significantly due to their diversified structures and distinct mesomorphic properties [10, 12]. Incorporation of heteroatoms results in considerable changes in the corresponding LC and physical properties, due to the fact that most of the heteroatoms (S, O and N) are more polarisable than carbon [13].

There are numerous accounts in the literature that describe the synthesis and mesomorphic behaviour of pyrazole-type compounds [14, 22]. Pyrazoles are the important five-membered heterocyclic compounds [23]. Pyrazole derivatives have attracted the attention of research scholars on account of their wide range of applications, pyrazoles have played a vital role in developing the theory in heterocyclic

chemistry and are also used extensively as useful synthons in organic synthesis [24]. Literature search reveals that formylation of hydrazones yields formyl pyrazoles. The Vilsmeier-Haack reaction (DMF/POCl₃) is a common method for the synthesis of 4-formyl pyrazoles [25]. In the present work we have formylated substituted acetophenone hydrazones which cyclize using Vilsmeier-Haack reagent to yield 4-formyl pyrazole derivatives. Then, the liquid crystalline properties were studied.

Experimental

The materials were taken from Aldrich, Fluka and Merck Co.

Techniques

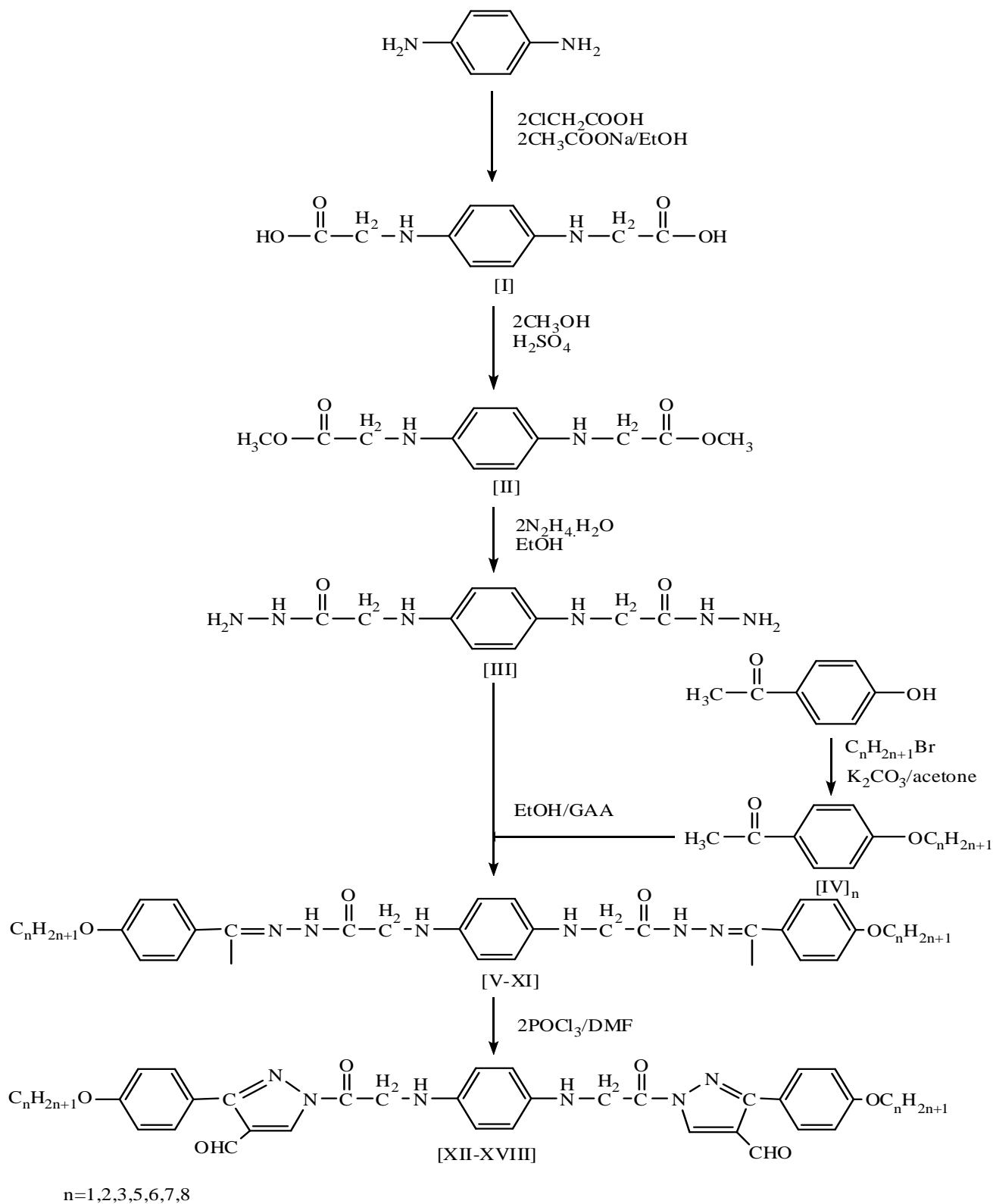
FT-IR spectra were recorded by SHIMADZU (IR Affinity-1) FT-IR spectrometer in the wave number range 4000-600 cm⁻¹. ¹H-NMR spectra were measured by Bruker, 400 MHz and were reported in ppm (δ), the compounds were dissolved in DMSO-d₆ solution with TMS as internal standard. The melting point was measured by Gallenkamp apparatus.

The textures of the mesophases were studied with POM model Leica DM2500 M. The samples were investigated using cross polarizers at room temperature with a magnification of 10× and a magnification 20× was at elevated temperature, the temperature initially was raised rapidly (5°C/min). Transition temperatures and

enthalpies were scanned in DSC measurements were conducted with STAPT-1000LINSIS with a heating rate of 5.0°C/min and it was calibrated with indium (156.6°C, 28.45J/g).

Synthesis

The route of synthesized new compounds is represented to Scheme1.



Scheme(1)

Synthesis of 2, 2'-(1, 4-phenylenebis (azanediy))diacetic Acid[I]

A mixture of 1,4-phenylenediamine (0.108gm,0.001 mol), chloro acetic acid (0.188 gm ,0.002 mol) and sodium acetate(0.16gm, 0.002mol) in ethanol(5mL).

The mixture was refluxed for (4 hrs). After cooling the mixture addition to ice water then filtration and acidified by 10%HCl after that, the ethyl acetate was added and separated the organic layer, dried and recrystallized from ethanol. Molecular formula $C_{10}H_{12}N_2O_4$, Yield 65 %, Color brown, M.P=99-101°C.

Synthesis of di methyl 2, 2'-(1, 4-phenylene bis (azanediy)) Diacetate [II]

In 200 mL absolute methanol added (55.158gm, 0.246mol) of compound [I] and (5.4mL) of sulfuric acid. The mixture was refluxed for 6hrs then cooled at room temperature after that added solution sodium bicarbonate 5% after that the precipeted filtered than washing in water [26] and recrystallized from ethanol. Molecular formula $C_{12}H_{16}N_2O_4$, Yield 80 %, Color dark brown, M.P >300 °C

Synthesis of 2, 2'-(1, 4-phenylene bis (azanediy)) di (acetohydrazide) [III]

To compound [II] (1.5gm , 0.006mol) added 3mL of hydrazine hydrate 80% then 5mL absolute ethanol the reaction mixture was refluxed for 3hrs then resulting solution was cooled to room temperature[27],dried and recrystallized from ethanol. Molecular formula $C_{10}H_{16}N_6O_2$, Yield 85 %, Color dark brown, M.P gummy general procedure of prepared 4-n-alkoxyacetophenone [IV]_n These compounds were prepared according to Williamson synthesis of ethers by a known method [28].

A mixture of 4-hydroxyacetophenone (0.204gm, 0.0015mol) and anhydrous potassium carbonate (0.8gm, 0.012mol) dissolved acetone 20mL, then n-alkylbromide (0.004mol) was added, the mixture was refluxed overnight. After word, the mixture was pouved onto ice water. The mixture was extracted by ethyl acetate and the organic phase was taken after that evaporated to yield 4-n-alkoxyacetophenone. The physical properties and characteristics FTIR absorption bands of compounds [IV]_n are listed in Table (1).

Synthesis of 2, 2'-(1, 4-phenylenebis (azanediy))bis(N'-(1-(4-alkoxyphenyl) ethylidene) acetohydrazide)[V-XI]

A mixture of acid hydrazide [III] (0.252g, 0.001mol) with 4-n-alkoxy acetophenone [IV]_n (0.002mol) and 5mL absolute ethanol with some drops from glacial acetic acid GAA, the solution heating for (4-5hrs) then cooled after that filtered and recrystallized from ethanol to give the compounds [V-XI]. The physical properties and characteristics FTIR absorption bands of compounds [V-XI] are listed in Table (2).

Synthesis of 1, 1'-(2, 2'-(1, 4-phenylene bis (azanediy)) bis (acetyl)) bis (3-(4-alkoxyphenyl)-1H-pyrazole-4-carbaldehyde) [XII-XVIII]

The compounds [V-XI] (0.01 mol) were added in mixture of Vilsmeier-Haack reagent (prepared by drop wise addition of 6mL of phosphorus oxychloride $POCl_3$ in ice cooled 50mL di methyl formamid DMF). The reaction mixture was refluxed for 6 hrs. After that the mixture was cooled and poured in to ice cold water, followed the solution neutralization with sodium bicarbonate then filtered to obtained the products. The physical properties and characteristics FTIR absorption bands of compounds [XII-XVIII] are listed in Table (3).

Results and Discussion

The syntheses of symmetric pyrazoles derivatives [XII-XVIII] are outlined in the Scheme 1.The compound [I] synthesized by reaction 1, 4-phenylenediamine with two moles chloro acetic acid, the FTIR spectrum for this compound showed disappearance of stretching bands of NH_2 groups of starting material and appearance of absorption stretching band at rang (3525 -3300) cm^{-1} of N-H and OH groups and C=O group of carboxylic moiety at (1728) cm^{-1} .

The compound [I] reaction with methanol in present sulfuric acid to synthesized ester compound [II]. FTIR spectrum for compound [II] showed disappearance of absorption bands of C=O and OH groups for carboxylic acid and showed stretching band at (1735) cm^{-1} for carbonyl C=O for ester group. After that reaction compound[II] with hydrazine hydrate to synthesized acide hydrazide [III] ,FTIR showed absorption stretching bands to asymmetric and symmetric of NH_2 and NH

groups in the region(3311-3197) cm^{-1} and stretching band at(1662) cm^{-1} to C=O amide group. Then the later compound reaction with substituted acetophenone[IV]_n that prepared from 4-hydroxy acetophenone by the Williamson's ether reaction with the corresponding alkyl bromides to synthesized substituted acetophenone hydrazones [V-XI]. The FTIR spectra for compounds [V-XI] showed the disappearance of a stretching band of NH² of acid hydrazide [III] and C=O (ketone) for 4-n-alkoxyacetophenone [IV]_n and showed absorption bands for(-N=CH) groups at region (1630-1610) cm^{-1} .

The ¹HNMR spectrum(in DMSO-d₆ as solvent) for compound [VII] showed: asinglet signal at δ 10.33 ppm for two protons of NH of (-CO NH -)groups, asinglet signal at δ 9.80 ppm for two protons of NH of (-NHCH₂-) groups, many signals at δ (7.84-6.84) ppm for twelve aromatic protons, signal at δ 3.99ppm for four protons of OCH₂ groups, signals at δ (2.48-2.09) ppm for protons of (-CH₂-) groups, asinglet signal at δ 1.76 ppm for six protons of two CH₃ groups and triplate signal at δ (1.49-0.85) ppm for six protons of two CH₃ groups(-CH₂CH₃).

In addition synthesized 4-formylpyrazole derivatives [XII-XVIII] via cyclisation substituted acetophenone hydrazones[V-XI] with Vilsmeier-Haack reagent DMF/POCl₃. The FTIR spectra of these compounds showed appearance bands at region (1708-1674) cm^{-1} assigned to C=O aldehyde group and absorption bands at region (1649- 1630) cm^{-1} for C=N group of pyrazole ring. The ¹HNMR spectrum(in DMSO-d₆ as solvent) for

compound [XII] showed: asinglet signal at δ 9.92 ppm for two protons of CH of (-CHO -) groups, asinglet signal at δ 8.63ppm for two protons NH of (-NHCH₂-), many signals at δ (7.93-6.83) ppm for twelve aromatic protons and two protons of pyrazole rings[29], asinglet signal at δ 3.81 ppm for six protons of OCH₃ groups, asinglet signal at δ 2.93ppm for four protons of (-CH₂-) groups.

Liquid Crystalline Properties

The phase 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). Phase identification was made by comparing the observed textures with those reported in the literature [30, 32].The Phase transition temperatures and phase assignment of series [V-XI] are summarized in Tables 4.

The compounds [V-VIII] showed enantiotropic nematic phase only as Figures 1(a) and 1(b) for compounds [V] and [VII], respectively, the DSC thermogram for compound [V] as Figure 2. While the compounds [IX] and [X] showed enantiotropic dimorphism smectic B phase besides to nematic phase as Figures 1(c) and 1(d) smectic B phase for compounds[IX] and [X], respectively, in addition to the compound [XI] showed enantiotropic smectic C phase and nematic phase. A plot of the transition temperature against the number (n) of carbon atoms in the alkoxy chain for compounds [V-XI] is shown in Figure 3.

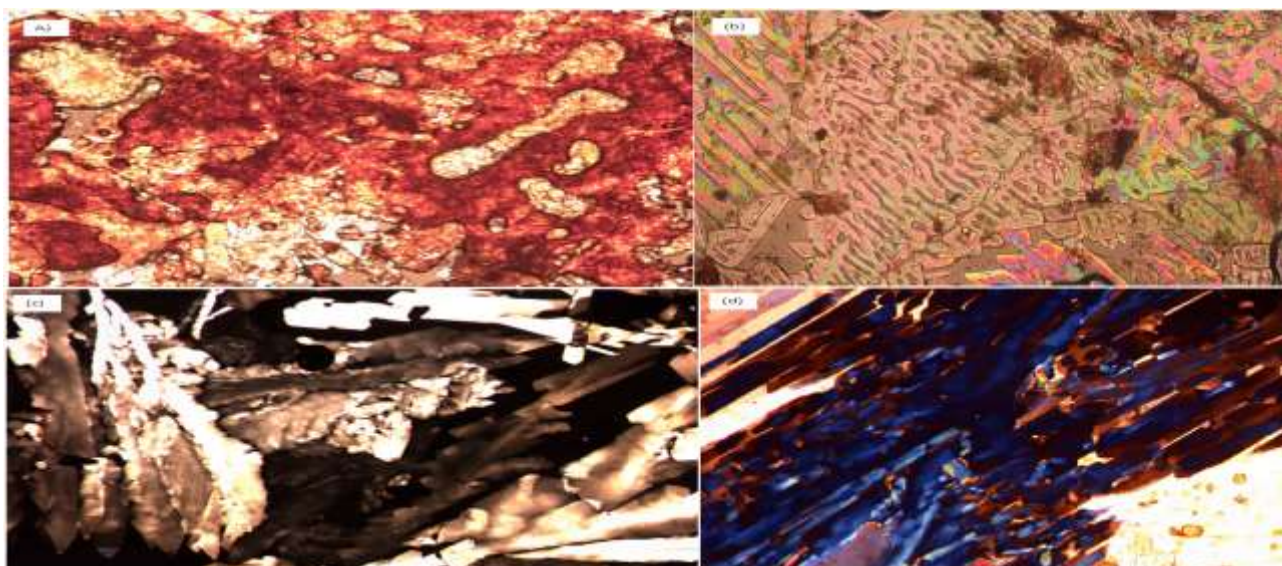


Figure 1: Cross polarizing optical textures of (a) Nematic phase For compound [V] at 203°C (b) Nematic thread-like texture for compound [VII] at 130 °C (c) smectic B phase for compound[IX] at 120°C (d) smectic B phase for compound[X] at 165°C

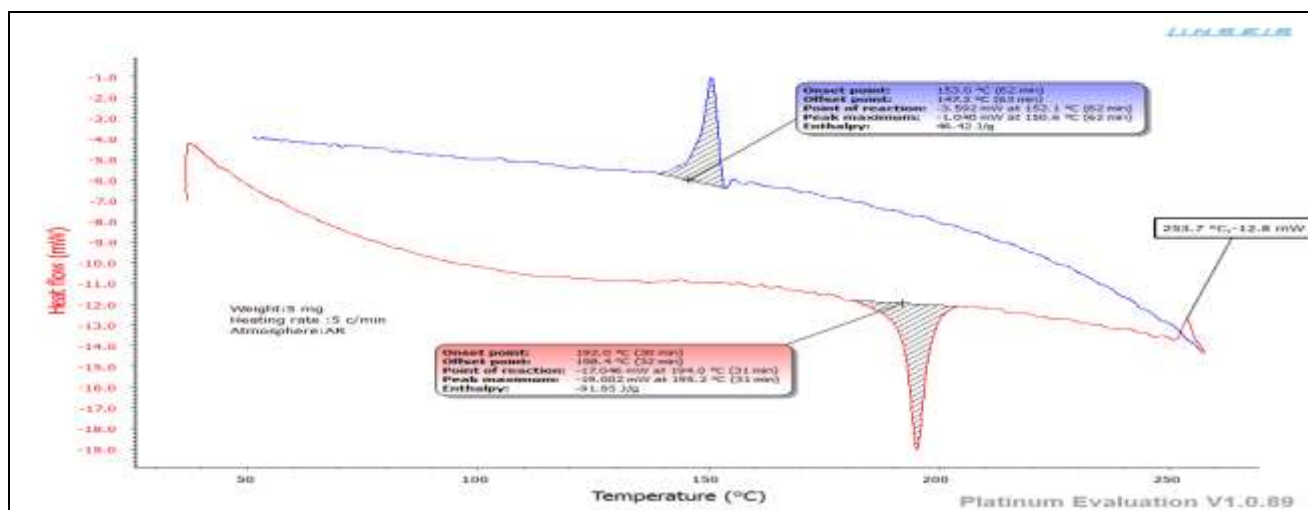
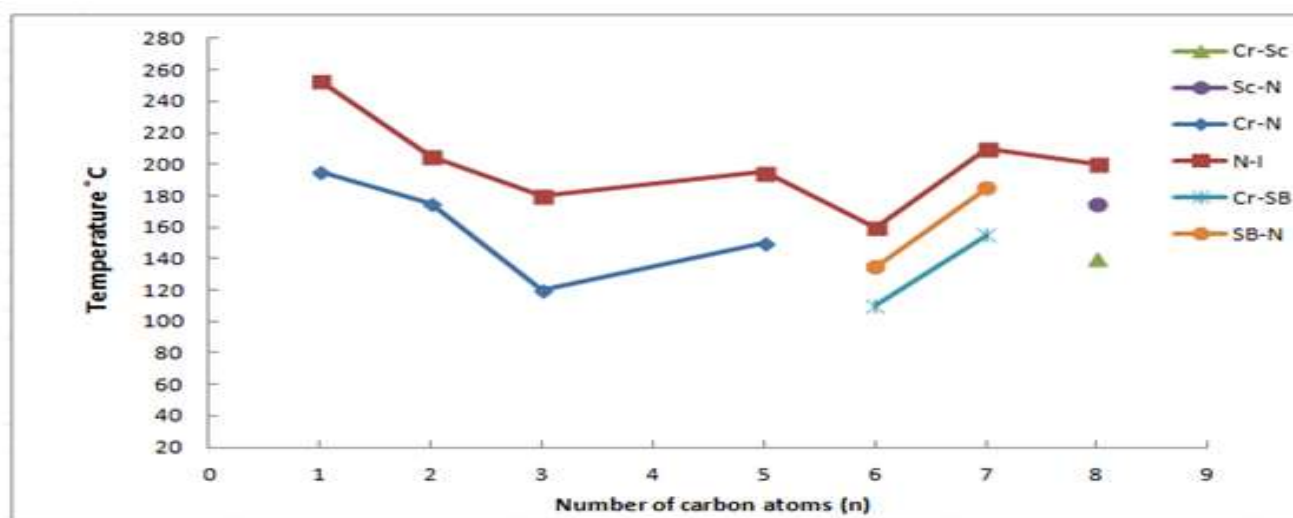


Figure 2: DSC thermo gram for compound [V]

Figure3: Dependence of transition temperatures on the increasing number of carbon atoms (n) in the terminal alkoxy chains for the [V-XI] series compoundsTable 1: The physical properties and characteristics FTIR absorption bands of compounds [IV] _n

Comp. No.	Nomenclature	Molecular formula	Yield %	M. P °C	Characteristic bands FTIR spectra(cm^{-1})				
					ν (C-H) arom.	ν (C-H) aliph.	ν (C=O) keto	ν (C=C) arom.	ν (C-O) ether
[IV] ₁	1-(4-methoxyphenyl) ethan-1-one	C ₉ H ₁₀ O ₂	78	32-34	3045	2964-2843	1672	1600	1225
[IV] ₂	1-(4-ethoxyphenyl) ethan-1-one	C ₁₀ H ₁₂ O ₂	70	gummy	3050	2983-2885	1668	1598	1249
[IV] ₃	1-(4-propoxyphenyl)ethan-1-one	C ₁₁ H ₁₄ O ₂	77	gummy	3060	2966-2877	1674	1597	1251
[IV] ₅	1-(4-(pentyloxy)phenyl) ethan-1-one	C ₁₃ H ₁₈ O ₂	72	28-30	3040	2966-2868	1676	1600	1259
[IV] ₆	1-(4-(hexyloxy)phenyl) ethan-1-one	C ₁₄ H ₂₀ O ₂	74	gummy	3055	2931-2862	1670	1597	1249
[IV] ₇	1-(4-(heptyloxy)phenyl) ethan-1-one	C ₁₅ H ₂₂ O ₂	78	40-42	3047	2945-2852	1672	1600	1244
[IV] ₈	1-(4-(octyloxy)phenyl) ethan-1-one	C ₁₆ H ₂₄ O ₂	70	gummy	3060	2954-2854	1676	1598	1253

Table 2: The physical properties and characteristics FTIR absorption bands of compounds [V-XI]

Comp. No.	Nomenclature	Molecular formula	Yield %	M. P °C	Characteristic bands FTIR spectra(cm ⁻¹)					
					ν (N-H)	ν (C-H) aro m.	ν (C-H) Aliph.	ν (C=O) amid	ν (C=N)	ν (C=C) aro m.
[V]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-methoxyphenyl)ethylidene)acetohydrazide)	C ₂₈ H ₃₂ N ₆ O ₄	75	156-158	3390	3010	2956-2837	1660	1627	1593
[VI]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-ethoxyphenyl)ethylidene)acetohydrazide)	C ₃₀ H ₃₆ N ₆ O ₄	73	162-164	3354	3025	2962-2850	1664	1630	1598
[VII]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-propoxyphenyl)ethylidene)acetohydrazide)	C ₃₂ H ₄₀ N ₆ O ₄	70	158-160	3300	3045	2962-2873	1670	1625	1593
[VIII]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-(pentyloxy)phenyl)ethylidene)acetohydrazide)	C ₃₆ H ₄₈ N ₆ O ₄	69	gum my	3356	3060	2935-2866	1664	1630	1593
[IX]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-(hexyloxy)phenyl)ethylidene)acetohydrazide)	C ₃₈ H ₅₂ N ₆ O ₄	75	gum my	3300	3035	2931-2862	1670	1610	1598
[X]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-(heptyloxy)phenyl)ethylidene)acetohydrazide)	C ₄₀ H ₅₆ N ₆ O ₄	70	gum my	3290	3050	2927-2858	1670	1615	1597
[XI]	2,2'-(1,4-phenylenebis(azanediyl))bis(N'-(E)-1-(4-(octyloxy)phenyl)ethylidene)acetohydrazide)	C ₄₂ H ₆₀ N ₆ O ₄	73	gum my	3330	3040	2924-2858	1670	1610	1597

Table 3: The physical properties and characteristics FTIR absorption bands of compounds [XII-XVIII]

Comp. No.	Nomenclature	Molecular formula	Yield %	M. P °C	Characteristic bands FTIR spectra(cm ⁻¹)					
					ν (N-H)	ν (C-H) aro m.	ν (C-H) aliph.	ν (C=O) alde.	ν (C=O) amid e	ν (C=N) endocycl ic
[XII]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-methoxyphenyl)-1H-pyrazole-4-carbaldehyde)	C ₃₂ H ₂₈ N ₆ O ₆	70	83-84	3390	3008	2935-2835	1674	1664	1635
[XIII]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-ethoxyphenyl)-1H-pyrazole-4-carbaldehyde)	C ₃₄ H ₃₂ N ₆ O ₆	68	102-105	3335	3035	2980-2883	1680	1666	1647
[XIV]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-propoxyphenyl)-1H-pyrazole-4-carbaldehyde)	C ₃₆ H ₃₆ N ₆ O ₆	65	95-97	3360	3060	2958-2858	1695	1665	1649
[XV]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-(pentyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)	C ₄₀ H ₄₄ N ₆ O ₆	73	gum my	3340	3040	2927-2866	1701	1670	1640
[XVI]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-(hexyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)	C ₄₂ H ₄₈ N ₆ O ₆	77	gum my	3330	3045	2927-2862	1708	1670	1630
[XVII]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-(heptyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)	C ₄₄ H ₅₂ N ₆ O ₆	68	gum my	3320	3060	2924-2858	1705	1670	1635
[XVIII]	1,1'-(2,2'-(1,4-phenylenebis(azanediyl))bis(ace tyl))bis(3-(4-(octyloxy)phenyl)-1H-pyrazole-4-carbaldehyde)	C ₄₆ H ₅₆ N ₆ O ₆	69	gum my	3335	3040	2930-2860	1698	1666	1642

Table 4: Phase transition temperatures of series [V-XI]

Comp. No.	Phase transition temperatures
[V]	$\text{cr} \xrightleftharpoons[150]{195} \text{N} \xrightleftharpoons[253]{} \text{I}$
[VI]	$\text{cr} \xrightleftharpoons[175]{} \text{N} \xrightleftharpoons[205]{} \text{I}$
[VII]	$\text{cr} \xrightleftharpoons[120]{} \text{N} \xrightleftharpoons[180]{} \text{I}$
[VIII]	$\text{cr} \xrightleftharpoons[150]{} \text{N} \xrightleftharpoons[195]{} \text{I}$
[IX]	$\text{cr} \xrightleftharpoons[110]{} \text{SmB} \xrightleftharpoons[135]{} \text{N} \xrightleftharpoons[160]{} \text{I}$
[X]	$\text{cr} \xrightleftharpoons[155]{} \text{SmB} \xrightleftharpoons[185]{} \text{N} \xrightleftharpoons[210]{} \text{I}$
[XI]	$\text{cr} \xrightleftharpoons[140]{} \text{SmC} \xrightleftharpoons[175]{} \text{N} \xrightleftharpoons[200]{} \text{I}$

Cr, crystalline phase; SmB smectic B phase ;SmC smecticC phase; N, nematic phase; I, isotropic liquid

Conclusions

In this study synthesized new homologues series containing pyrazole unit with alkoxy chain. The shorter alkoxy group exhibit nematic liquid crystalline behavior, while the

longer alkoxy group homologue shows smectic and nematic liquid crystal property. The homologous series shows nematogenic and smectogenic behavior with good thermal stability.

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