

Synthesis, Characterization, and Mesomorphic Properties of New Pyridine Derivatives

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Introduction

The field of liquid crystals (LCs) is now well established not only in basic research but also in the development of new applications and their commercial use. As LCs represent an intermediate state between ordinary liquids and solids, the investigation of their physical properties is very complex and hence their study requires the use of many different tools and techniques. The fundamental requirement for any substance to exhibit a liquid crystalline phase is the shape anisotropy of the constituent molecules.

LCs play important roles in materials science, and they are model materials for organic chemist to investigate the relationship between the chemical structure and physical properties. In recent years, significant attention has been given to the development of new LC materials for novel areas such as thin-film transistors (TFT), organic light-emitting diodes (OLED), solid organic lasers and photovoltaic devices; this is mainly due to the self-assembling properties and the various supramolecular structures of liquid crystals.

Organic LC materials constitute aromatic or heteroaromatic systems carrying different linking groups and terminal substituents. Generally, these organic LCs can be designed and constructed using various aromatic or heteroaromatic systems to fulfill the criteria for the desired applications. In this respect, benzene, biphenyl, anthracenyl and phenanthrenyl moieties have been most commonly explored as the aromatic core.

Heterocyclic LCs contain a heterocycle as the core moiety. Precisely, a heterocyclic compound is one that contains a ring made up of one or more heteroatom, such as nitrogen, oxygen or sulfur, in addition to carbon. Generally, the design of novel thermotropic LCs involves the suitable selection of a core fragment, linking group and terminal functionality. Over many years, a large number of LCs containing heterocyclic units as core moieties have been synthesized. Modern synthesis techniques allow researchers to access tailor-made compounds with predictable properties, in the development of new LC materials. The incorporation of heterocyclic moieties as core units in thermotropic LCs can result in large changes in their mesophases and physical properties, because they possess more polarizable heteroatoms, such as nitrogen, oxygen and sulfur atoms in their structure. In this aspect, the development of new LC materials bearing heterocyclic rings such as pyridine, pyrimidine, pyrazole, imidazole, oxadiazole and benzothiazole are of great interest, as they impart long range mesogenic stability to the resulting LCs.

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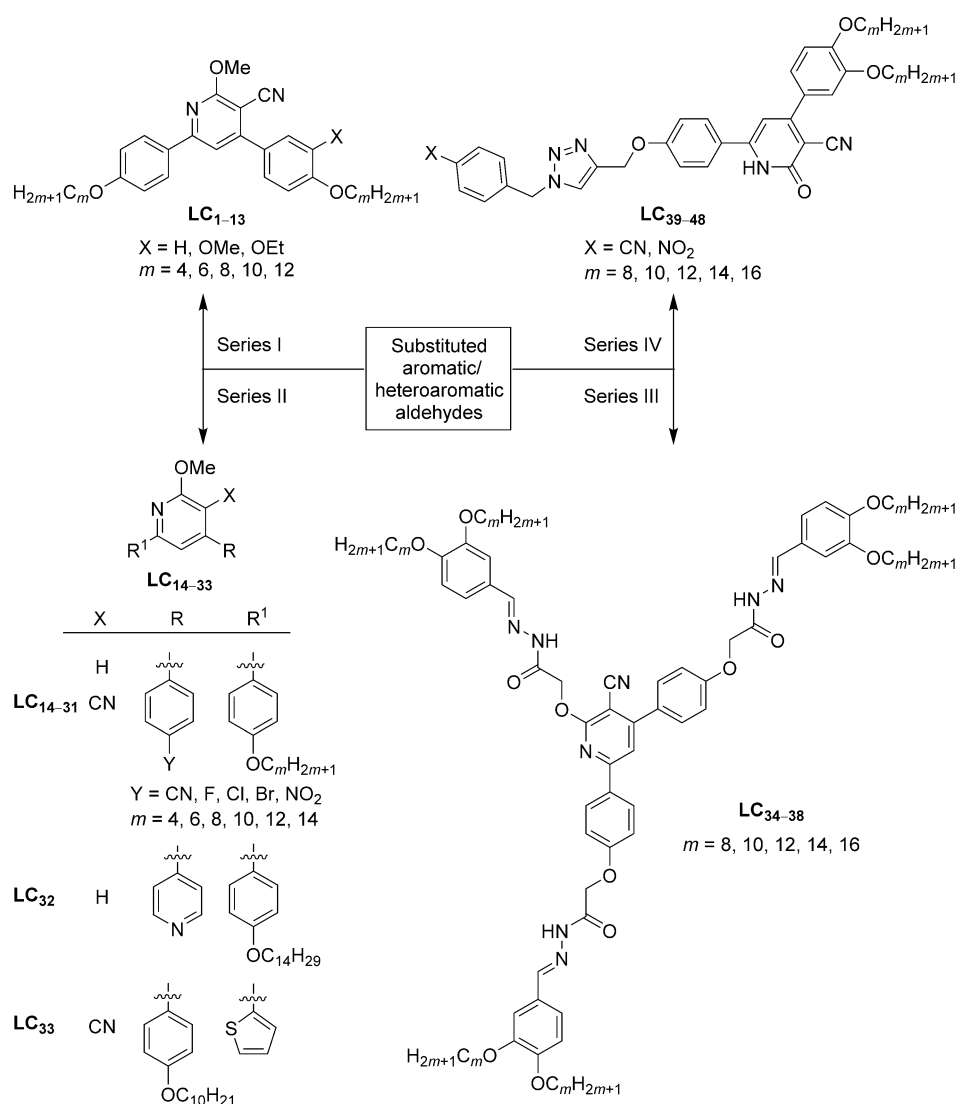
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Amongst various heterocyclic LCs, pyridine-based mesogens have gathered much interest because the presence of the pyridine moiety not only imparts rigid stable structure but also induces complex LC phases in the resulting molecules. Also, it adds a wide range of photophysical properties. Given their importance, the doctoral research described here mainly focused on design and synthesis of new pyridine-based LCs.

Design of Pyridine Derivatives

On the basis of literature reports, four new series of pyridine derivatives were designed. The first series was designed by taking an electron-deficient core, 2-methoxy-3-cyanopyridine, as an acceptor unit and an electron-rich alkyloxyphenyl unit as a donor group to form D-A type molecular architecture (Series I; LC₁₋₁₃). In the design of the second series, methoxypyridine/2-methoxy-3-cyanopyridine was selected as a core and substituted aryl/heteroaryl moieties as terminal groups in order to create molecules with an unsymmetrical "bent" shape (Series II; LC₁₄₋₃₃). The third series containing new disc shaped 2-(4,6-disubstituted aryl-3-cyanopyridyl)oxyacetohydrazone were designed (Series III; LC₃₄₋₃₈). Finally, the fourth series was designed by connecting a 1,4-disubstituted 1,2,3-triazole unit with a luminescent 3-cyanopyridone ring in order to obtain a novel molecular architecture (Series IV; LC₃₉₋₄₈). The

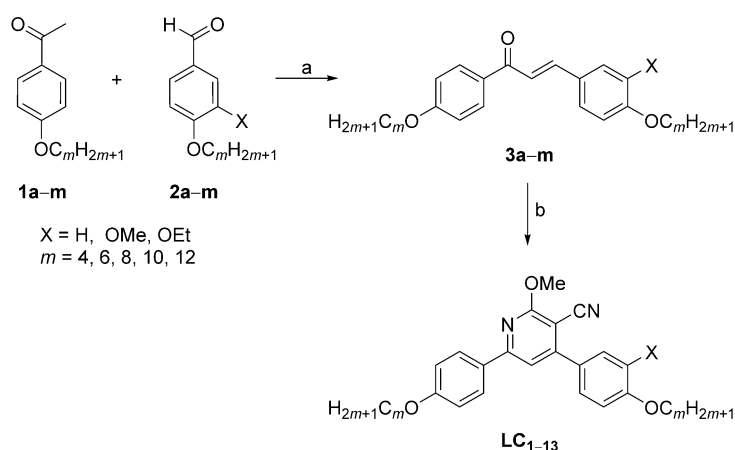


Scheme 1. Summary of new pyridine derivatives LC₁₋₄₈.

hope was that the newly designed compounds (Scheme 1) would exhibit liquid crystalline behavior at ambient temperature as well as improved photophysical properties.

Synthesis and Characterization

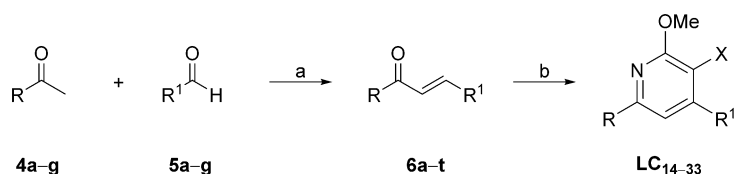
Series I–IV were successfully synthesized following appropriate synthetic routes. The target compounds of Series I were synthesized according to Scheme 2. The required starting materials alkoxyacetophenones **1a–m** and alkoxybenzaldehydes **2a–m** were prepared in good yield by O-alkylation of 4-hydroxyacetophenone and 4-hydroxybenzaldehyde or *meta*-substituted 4-hydroxybenzaldehyde by reacting with the corresponding alkyl bromides according to a reported procedure. Required dialkoxyarylprop-2-en-1-one **3a–m** were prepared from **1a–m** and **2a–m** using a Claisen–Schmidt reaction. It was then cyclized to obtain 4,6-dialkoxyaryl-2-methoxy nicotinonitriles **LC_{1–13}** by reacting them with malononitrile in presence of sodium methoxide.



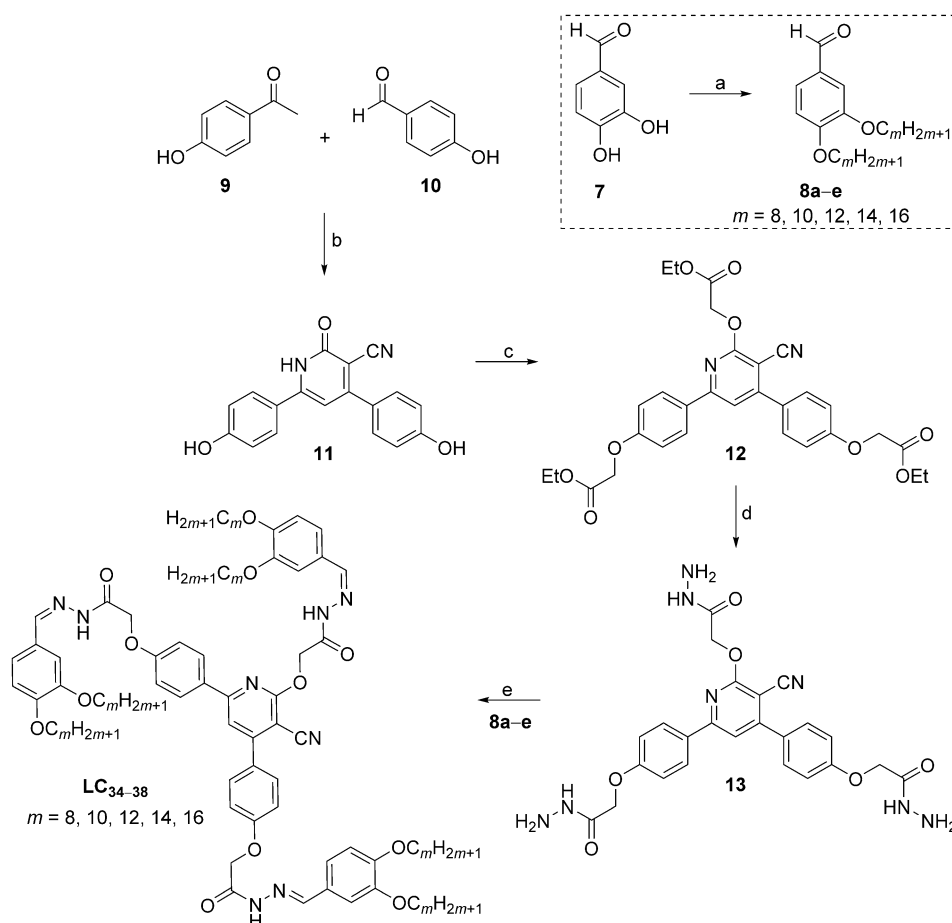
Scheme 2. Synthesis of 4,6-dialkoxyaryl-2-methoxy nicotinonitriles (Series I; **LC_{1–13}**). Reagents and conditions: a) aq KOH (1.2 equiv), EtOH, rt, 4 h, 68–83%; b) Malononitrile, NaOMe, MeOH, rt, 4 h, 62–82%.

The synthetic route for the preparation of the target compounds of Series II are shown in Scheme 3. The starting materials (**4a–g**) were prepared in good yield by reacting various alkyl bromides ($m=4, 6, 8, 10, 12, 14$) with 4-hydroxyacetophenone according to the reported procedure. The required prop-2-en-1-ones (**6a–t**) were prepared from aryl or heteroaryl ketones (**4a–g**) and aryl or heteroaryl aldehydes (**5a–g**) using a Claisen–Schmidt reaction. Further, it was cyclized to obtain 6-alkoxyaryl/thiophenyl-4-substituted aryl-2-methoxy pyridines derivatives (**LC_{14–33}**) by reacting it with malononitrile in presence of sodium methoxide at room temperature. It has been well-established that prop-2-en-1-one upon reacting with malononitrile in basic medium (i.e., sodium methoxide) cyclizes to 2-methoxy-3-cyanopyridine via dehydrogenation. Further, prop-2-en-1-ones (**6a–f, m–s**), upon reacting with malononitrile in basic medium, readily cyclizes to methoxypyridines (**LC_{14–19, 26–32}**) via dehydrocyanation.

The synthetic route for the preparation of **LC_{34–38}** (Series III) is illustrated in Scheme 4. The required 3,4-bis(alkoxy)benzaldehydes (**8a–e**) were prepared by O-alkylation of 3,4-dihydroxybenzaldehyde (**7**) with the appropriate alkyl bromides. On the other hand, compound **11** was prepared by a one-pot reaction of 4-hydroxyacetophenone (**9**) and 4-hydroxybenzaldehyde (**10**) with ethyl cyanoacetate in the



Scheme 3. Synthesis of new 6-alkoxyaryl/thiophenyl-4-substituted aryl-2-methoxy pyridines. Reagents and conditions: a) aq KOH (1.2 equiv), EtOH, rt, 4 h, 66–85%; b) Malononitrile, NaOMe, MeOH, rt, 4 h, 46–82%.



Scheme 4. Synthesis of new 2-(4,6-disubstituted aryl-3-cyanopyridyl) oxy acetohydrazones (**LC**₃₄₋₃₈). *Reagents and conditions:* a) alkyl bromide, anhyd K₂CO₃, DMF, 80 °C, 12 h, 82–88%; b) ethyl cyanoacetate, ammonium acetate, 1,4-dioxane, reflux, 12 h, 62%; c) ethyl chloroacetate, anhyd K₂CO₃, DMF, 80 °C, 12 h, 71%; d) NH₂NH₂·H₂O, EtOH, reflux, 12 h, 48%; e) AcOH (few drops), EtOH, reflux, 12 h, 61–73%.

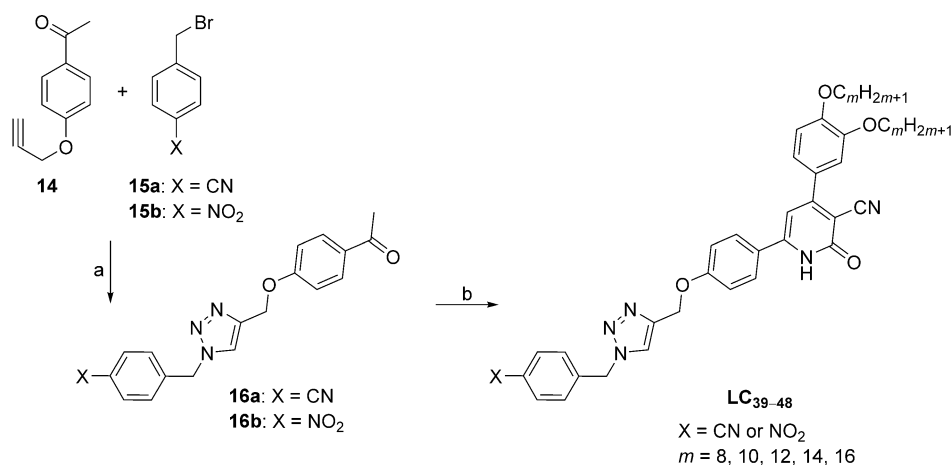
presence of excess ammonium acetate with 1,4-dioxane as the solvent. Furthermore, the reaction of intermediate **11** with ethyl chloroacetate and anhydrous potassium carbonate in dry dimethylformamide afforded tri-ester-functionalized compound **12** in good yield (71%). The reaction of compound **12** with hydrazine hydrate in refluxing ethanol gave trihydrazide **13**. Finally, trihydrazide derivative **13** was condensed with substituted benzaldehyde **8a–e** in the presence of glacial acetic acid as a catalyst in order to obtain target trihydrazone-functionalized cyanopyridines **LC**₃₄₋₃₈.

The synthetic route for the preparation of target compounds **LC**₃₄₋₄₈ (Series IV) is shown in Scheme 5. Acetyl-functionalized 1,4-disubstituted 1,2,3-triazole intermediate **16** was prepared from a one-pot reaction between 4-propargyloxyacetophenone **14** and 4-substituted benzylbromide **15** via a little modified Click reaction in ethanol/water. The other intermediate, 3,4-bis(alkoxy)benzaldehyde (**8**), was prepared by reacting 3,4-dihydroxybenzaldehyde with various alkylbromides using the Williamson method. Furthermore, cyanopyridone derivatives **LC**₃₉₋₄₈ were prepared by a one-pot reaction of acetyl-functionalized 1,2,3-triazole **16** and 3,4-bis(alkoxy)benzaldehyde **8** with ethyl cyanoacetate in the presence of ammonium acetate in 1,4-dioxane.

All newly synthesized compounds were characterized by Fourier transform infrared spectroscopy (FTIR), ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. The structures of a select few compounds were also confirmed by single-crystal X-ray diffraction (SCXRD) analysis.

Mesogenic, Optical, and Optoelectronic Properties

Mesogenic properties of newly synthesized target compounds were investigated by using polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction (PXRD)



Scheme 5. Synthetic route for the synthesis of target compounds LC₃₉₋₄₈. *Reagents and conditions:* a) NaN₃, CuI (10 mol%), EtOH/H₂O (1:1), 80 °C, 12 h, 69–76%; b) 8a–e (see Scheme 4 for synthesis), ethyl cyanoacetate, ammonium acetate, 1,4-dioxane, reflux, 12 h, 64–83%.

studies. Amongst the 48 compounds, almost all the compounds exhibit LC phases; LC₁, LC₁₄, and LC₂₀₋₂₅ show nematic phases. The observed nematic phase in compounds LC₁ and LC₁₄ is due to the presence of a polar cyano group and lower alkoxy chains (butoxy) in their structure. Compounds LC₂₀₋₂₅ display nematic phase; this is mainly because of the presence of a lateral cyano group as well as a fluoro or chloro group and variable alkoxy chains as terminal substituents.

Compounds LC₂₋₁₃ and LC₂₆₋₃₃ show rectangular columnar phase. Appearance of ambient temperature rectangular columnar phase in compounds LC₂₋₁₃ is attributed to the strong intermolecular interactions and the effect of higher alkoxy chains in them, while the presence of elevated temperature rectangular columnar phase in compounds LC₂₆₋₃₃ is mainly due to the effect of nitro, bromo or 4-pyridinyl groups and variable alkoxy chains as terminal substituents.

Compounds LC₁₅₋₁₉ exhibit orthorhombic columnar phase at an elevated temperature (99–125 °C) owing to the presence of a polar cyano group and higher alkoxy chains. Compounds LC₃₄₋₃₈ and LC₃₉₋₄₈ show hexagonal columnar phase at ambient temperature. The formation of mesophase in compounds LC₃₄₋₃₈ is due to the existence of intermolecular hydrogen bonds and π - π interactions exerted by the cyanopyridine core as well as variable alkoxy chain lengths. While, the observed mesophase in compounds LC₃₉₋₄₈ can be attributed to the presence of terminal polar substituents (i.e., CN or NO₂) and variable alkoxy chain lengths. Also, the hydrogen bond ability of cyanopyridone moiety together with the planar 1,2,3-triazole unit contribute significantly in the formation of the observed mesophase.

Photophysical properties of target compounds were evaluated by using UV-visible and fluorescence spectrometry. UV-visible absorption and fluorescence emission spectra of LC₁₋₄₈ show a strong absorption band in the range of 320–370 nm and a strong blue emission band in the range of 380–470 nm. The blue light emission is mainly due to the presence of π - π^* electronic transition. The solvent-dependent fluorescence emission study of LC₁ reveals that the blue emission bands shift to higher wavelength (positive solvatochromism) with the variation of organic solvents (nonpolar to polar). The fluorescence spectra of LC₂₋₁₃ in solution show blue emission band in the range of 398–415 nm, and these bands are slightly red shifted by 6–12 nm in the liquid crystalline film state. Also, the compounds exhibit good quantum yields ($\Phi_f = 28$ –49%) in the solution state and satisfactory quantum yields ($\Phi_f = 10$ –22%) in the film state also. The fluorescence emission spectra of LC₁₄₋₁₉, LC₃₄₋₃₈ and LC₃₉₋₄₈ display emission bands in the range of 380–466 nm ($\Phi_f = 42$ –60%) in the solution state and emission bands in the range of 434–480 nm in the film state. Finally, the optoelectronic study was carried out on a single-layer device with device structure ITO/LC₃₈/LiF (1 nm)/Al (110 nm) under dark as well as UV and white-light illuminations. The optoelectronic results reveal that LC₃₈ is an active photo-responsive and electron-transporting material for device applications.

Keywords: cyanopyridines · cyanopyridones · liquid crystals · methoxy-pyridines · solvatochromism

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