Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Role of Terminal Heterocyclic Ring on Mesomorphic Properties of Homologous Series*

B. T. Thaker [a], B. S. Patel [a], D. B. Solanki [a], Y. T. Dhimmer [a] & J. S. Dave [b]

[a] Department of Chemistry, Veer Narmad South Gujarat University, Surat, Gujarat, India

[b] Department of Applied Chemistry, Faculty of Technology and Engineering, M. S. University of Baroda, Vadodara, Gujarat, India

Version of record first published: 01 Mar 2010

To cite this article: B. T. Thaker, B. S. Patel, D. B. Solanki, Y. T. Dhimmer & J. S. Dave (2010): Role of Terminal Heterocyclic Ring on Mesomorphic Properties of Homologous Series*, Molecular Crystals and Liquid Crystals, 517:1, 63-80

To link to this article: http://dx.doi.org/10.1080/15421400903290501

Mol. Cryst. Liq. Cryst., Vol. 517: pp. 63–80, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903290501

Taylor & Francis
Taylor & Francis Group

Role of Terminal Heterocyclic Ring on Mesomorphic Properties of Homologous Series*

B. T. THAKER,[1] B. S. PATEL,[1] D. B. SOLANKI,[1]
Y. T. DHIMMER,[1] AND J. S. DAVE[2]

[1]Department of Chemistry, Veer Narmad South Gujarat University,
Surat, Gujarat, India
[2]Department of Applied Chemistry, Faculty of Technology and
Engineering, M. S. University of Baroda, Vadodara, Gujarat, India

Two new homologous series of compounds with a heterocyclic ring having sulfur and oxygen as a hetero atom derived from p-hydroxy acetophenone and alkoxy aniline containing cinnamate-azomethine as central linkages have been synthesized. viz. 4(furalacryloxy) α-methyl benzylidine-4′-alkoxy aniline and 4(thianylacryloxy) α-methyl benzylidine-4′-alkoxy aniline. The compound of both the series have been characterized by elemental analysis, FT-IR, ^{1}H-NMR, and mass spectrometry method. Their liquid crystalline properties have been investigated by optical polarizing microscopy and differential scanning calorimetry (DSC) studies. All the derivatives are mesomorphic in nature showing the nemetic phase. The mesomorphic properties of the present two series are compared with other structurally related series to evaluate the effect of thiophene and furan on mesomorphism.

Keywords Azomethine; central linkage; cinnamate; heterocyclic ring; homologous series; nematic mesophase

1. Introduction

The liquid crystalline properties of organic compounds are highly sensitive to changes in chemical structure, and considerable effort has been devoted to the systematic study of closely related compounds in order to establish empirical relationships between structural and other parameters and the thermal stabilities of the various types of mesophase which may be observed [1]. The design and synthesis of liquid crystals containing heterocyclic units have been the subject of much research in recent years [2–7]. Due to greater choices in the design of new mesogenic molecules containing heterocyclic rings, the polarity and geometry of the molecules may be varied by the introduction of heteroatoms [8,9]. There have been many

---

*This paper has been presented in ICFMAT, during 29–30th January, 2009 at Department of Physics, Velammal Engineering College, Ambattur – Redhills Road, Chennai – 600 066, Tamil Nadu, India.

Address correspondence to B. T. Thaker, Department of Chemistry, Veer Narmad South Gujarat University, Udhana-Magdalla Road, Surat 395007, India. E-mail: btthaker1@yahoo.co.in attempts made to introduce an oxygen and sulfur atom into the molecular rigid core for liquid crystalline derivatives which are suitable for use as components of nemetic liquid crystalline materials [10,11]. The 2,5-disubstituted thiophene ring is a potentially useful element of the molecular structure of new nematic liquid crystals due to a number of factors [12,13]. Liquid crystals derived from thiophene, a five member heterocycle comprising sulfur, are interesting because they deviate from the classical calamitic structure inducing looser packing and thus lowering the melting point. The electronegative sulfur atom imparts a transverse dipole, and the ring itself is a rich source of polarizable electrons, which may be useful for electro-optic applications [14–16]. Sulfur-containing heterocycles are important synthetic intermediates and have a variety of applications in medicinal, agricultural, and materials chemistry [17,18]. The heterocyclic mesogens reported so far mainly have nitrogen as a heteroatom [19,20] and mesomorphic compounds with oxygen as a heteroatom [21–23] are rare.

The systematic study of the mesogenic properties of a thio and oxo heterocyclic system would be interesting. Nguyen and Pham [24] have synthesized simple Schiff bases with 2-substituted furan derivatives. Cinnamate esters have been well known for over 30 years [25–27]. The ethylene linking group is a very useful structural unit connecting one part of a rigid core with another in calamitic mesogen molecules. The molecular structure of calamitic liquid crystals varies, and consequently, their mesomorphic properties differ significantly [28]. The polarity and the size of heteroatom affects the mesomorphic properties of a homologous series, and hence it was thought useful to evaluate oxo and sulfur heteroatom liquid crystals. The present investigation was undertaken with a view to study the effect of α-methyl group (azomethyne linkage) and heterocyclic moiety on the mesomorphic properties of such molecules.

2. Experimental

2.1. *Reagents and Technique*

The solvents were used after purification, using the standard methods described in the literature [29]. 4-Hydroxy acetanilide, p-hydroxy acetophenone were obtain from Merck (Germany). Furan 2-aldehyde, thiophene 2-aldehyde, alkyl bromide, and malonic acid were purchased from Fluka Chemie (Switzerland). Other auxiliary chemicals were laboratory grade. Elemental analyses (C, H, N) performed at CDRI, Lucknow. Infrared spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrophotometer in the frequency range 4000–400 cm^{-1} with samples embedded in KBr discs. ^{1}H-NMR spectra of the compounds were recorded with a Jeol-GSX-400 instrument using $CDCl_3$ as a solvent and TMS as an internal reference at SAIF, Panjab University, Chandigarh. Mass spectra of the compounds were recorded at SAIF, IIT Madras, Chennai. Thin-layer chromatography (TLC) analyses were performed using aluminium-backed silica-gel plates (Merck60 F524) and examined under shortwave UV light. The phase-transition temperatures were measured using ShimadzuDSC-50 at heating and cooling rates of 10°C min^{-1}, respectively. The optical microscopy studies were carried out with a Carl Zeiss polarizing microscope equipped with a MettlerFP52 hot stage. The textures shown by the compounds were observed using polarized light with crossed polarizers with the sample in a thin film sandwiched between a glass slide and cover slip.

2.2. *Synthesis*

Series: I-Me

2.2.1. *Synthesis of 4-n alkoxy anilines [30–32]*

(I) [a] 4-*n* Alkoxy Acetanilides:

Paracetamol (0.1 mole), anhydrous potassium carbonate (0.15 mole), respectively n-alkayl bromide (0.15 mole) and dry acetone (60 ml) were taken in RBF provided with condenser and guard tube. The reaction mixture was refluxed on water bath for (8–10 hrs). The whole mass was then added to water and extracted with ether. The ether was evaporated, and the residual solids were obtained as alkoxy acetanilides.

[b] 4-*n* Alkoxy Anilines:

A mixture of 4-*n* alkoxy acetanilide (0.146 mole), water (70 ml), and concentrated hydrochloric acid (45 ml) were stirred for 10 to 12 hrs at 90–95°C and then cooled to room temperature. The mixture was made alkaline with 50% NaOH at 20°C. The oily product (for the lower members C_1 to C_8) was extracted with ether. The ether extract was dried and concentrated at reduced pressure to give an oil which was purified by distillation. The higher members (C_{10} to C_{18}) separated as solid and were filtered directly without ether extraction. The boiling points and melting points of all the alkoxy anilines agree well with the values reported in the literature [30–32].

(II) Synthesis of Furylacrylic Acid [33]

Redistilled furfural (0.1 mol, 8.3 ml) and malonic acid (0.15 mol, 15.6 gm) were condensed in presence of dry pyridine (20–25 ml) by using few drops of piperidine as a condensing agent. The reaction mixture was heated on a steam-bath for 6 to 8 hrs. It was acidified with cold 1:1 hydrochloric acid, the precipitated acid was filtered and washed with little cold hydrochloric acid, followed by cold water. The acid was crystallized to fine white needles using with dilute ethanol as solvent. Melting point 140°C. The yield was about 70%.

(III) Synthesis of Furylacryloyl Chloride [34]

Furylacrylic acid (0.01 mole, 1.4 gm) and freshly distilled thionyl chloride (0.03 mole, 2.19 ml) were taken in around bottom flask attached with a reflux condenser fitted with a calcium chloride guard tube. The mixture was refluxed on water bath till evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using vacuum pump and the furylacryloyl chloride left behind, directly treated for next reaction without further purification.

(IV) Synthesis of 4(Furylacryloyloxy) Acetophenone

4-Hydroxy aetophenone (0.01 mole, 1.36 gm) was dissolved in dry pyridine (10.0 ml) and was added drop wise with occasionally stirring into ice-cold furylacryloyl chloride (0.01 mole, 1.71 gm) in a round bottom flask. Then mixture was refluxed on hot water bath for two hours and was allowed to stand for overnight. The mixture was acidified with cold 1:1 diluted hydrochloric acid to precipitate the product. The obtained solid was filtered, washed successively with saturated $NaHCO_3$ solution, dilute NaOH solution, and two to three times with water. Thus crude solid was obtained which was crystallized from water until the constant melting temperatures was obtained.

(V) Synthesis of 4(Furylacryloyloxy) α-Methyl Benzylidene-4′-*n*-Alkoxyanilines
A mixture of 4(furylacryloyloxy) acetophenone (0.01 mole) and respective alkoxy aniline (0.01 mole) and three drops of acetic acid in absolute ethanol (10 ml) was refluxed for 4 hr. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The solid was collected, yield 75%. All the compounds have been purified by column chromatography on silica gel (80–120 mesh) using mixture of ethyl acetate/petroleum ether [7/3] followed by repeated recrystallization from ethanol. Melting points and other thermal properties of all the compounds (C_1 to $C_{8,}$ C_{10} to C_{18}) are recorded in Table 1.

Analytical Data for a Few Respective Compounds

Series: I-Me [A-10]Molecular formula: $C_{32}H_{39}NO_4$ *(501).* **Elemental analysis** calculated for C 76.70%, H 7.83%, N 2.85%; found C 76.54%, H 7.67%, and N 2.71%; **FT-IR (KBr pellet)**: 3092 cm^{-1} (-C-H Aromatic), 2970, 2881 cm^{-1} (-CH_3CH_2 asymmetric ν_{as} and symmetric ν_s stretching, respectively), 1735 cm^{-1} (C=O group of cinnamate linkage), 1640 cm^{-1} (C=N stretching of Schiff base linkage), 1498 cm^{-1} (C=C stretching aromatic ring) **^{1}H-NMR ($CDCl_3$)**: 0.86–0.89 ppm (t, 3 H, CH_3 of aliphatic chain), 1.25–1.76 ppm (m, (-CH_2)n- of alkoxy chain), 2.17 ppm (S, 3H, CH_3 of acetophenone), 4.03–4.08 ppm (t, 2 H, -OCH_2 of alkoxy chain), 6.40 and 7.72 ppm (d, 2 H, -CH=CH- of cinnamate), 6.62–6.78 ppm (m, Ar-H). **FAB mass spectra:** Molecular ion peak 501 (m/z, M$^+$).

Series: II-Me

(I) Synthesis of 4-*n*-Alkoxy Anilines
4-*n*-Alkoxy anilines have been prepared as described in Series: I-Me (I).

(II) Synthesis of Thionylacrylic Acid
Thionylacrylic acid was prepared as per the procedure given in Series: I-Me (II). Melting point 146°C. The yield was 70%.

(III) Synthesis of Thionylacryloyl Chloride
Synthesis of thionylacryloyl chloride was carried out as per the procedure given in Series: I-Me (III).

(IV) Synthesis of 4(Thionylacryloyloxy) Acetophenone
4-Hydroxy acetophenone (0.01 mole, 1.36 gm) was dissolved in dry pyridine (10.0 ml) and was added drop wise with occasionally stirring into ice-cold thionylacryloyl chloride (0.01 mole, 1.88 gm) in a round bottom flask. Then mixture was refluxed on hot water bath for two hours and was allowed to stand for overnight. The mixture was acidified with cold 1:1 diluted hydrochloric acid to precipitate the product. The solid obtained was filtered, washed successively with saturated $NaHCO_3$ solution, dilute NaOH solution, and two to three times with water thus crude solid was obtained which was crystallized from water until the constant melting temperatures was obtained.

(V) Synthesis of 4(Thionylacryloyloxy) α-Methyl Benzylidene-4′-*n*-Alkoxyanilines
A mixture of 4-(thionylacryloyloxy) acetophenone (1 mole) and respective alkoxy aniline (1 mole) and three drops of acetic acid in absolute ethanol (10 ml) was refluxed for 4 hrs. The reaction mixture was allowed to cool and was stirred at room temperature overnight. The solid was collected, yield 76%. All the compounds have been purified by column chromatography

Table 1. Data table of the elemental analysis for the Series: I-Me

Comp. code no.	Molecular formula	Mol. wt g/mol	M.P.C	% Yield	Color	R_f Value	Analysis (%), Found (calculated)		
							C	H	N
A_1	$C_{23}H_{21}NO_4$	375	210	75	Yellow	0.80	73.60 (73.66)	5.60 (5.64)	3.73 (3.76)
A_2	$C_{24}H_{23}NO_4$	389	214	68	Yellow	0.84	74.03 (74.06)	5.91 (5.96)	3.59 (3.64)
A_3	$C_{25}H_{25}NO_4$	403	196	74	Yellow	0.81	74.44 (74.50)	6.20 (6.24)	3.47 (3.52)
A_4	$C_{26}H_{27}NO_4$	417	202	70	Yellow	0.87	74.82 (74.88)	6.47 (6.52)	3.35 (3.39)
A_5	$C_{27}H_{29}NO_4$	431	173	73	Yellow	0.81	75.17 (75.25)	6.72 (6.75)	3.24 (3.31)
A_6	$C_{28}H_{31}NO_4$	445	186	76	Yellow	0.77	75.50 (75.56)	6.96 (6.99)	3.14 (3.18)
A_7	$C_{29}H_{33}NO_4$	459	160	78	Yellow	0.87	75.81 (75.84)	7.18 (7.23)	3.05 (3.08)
A_8	$C_{30}H_{35}NO_4$	473	148	80	Yellow	0.82	76.10 (76.17)	7.39 (7.43)	2.95 (2.98)
A_{10}	$C_{32}H_{39}NO_4$	501	114	76	Yellow	0.91	76.54 (76.70)	7.67 (7.83)	2.71 (2.85)
A_{12}	$C_{34}H_{43}NO_4$	529	109	73	Yellow	0.83	77.12 (77.18)	8.12 (8.15)	2.64 (2.67)
A_{14}	$C_{36}H_{47}NO_4$	557	107	75	Yellow	0.83	77.55 (77.62)	8.43 (8.46)	2.51 (2.56)
A_{16}	$C_{38}H_{51}NO_4$	585	106	72	Yellow	0.89	77.94 (78.01)	8.71 (8.77)	2.39 (2.44)
A_{18}	$C_{40}H_{55}NO_4$	613	103	76	Yellow	0.78	78.30 (78.33)	8.97 (9.04)	2.28 (2.93)

Table 2. Data table of the elemental analysis for the Series: II-Me

Comp. code no.	Molecular formula	Mol. wt g/mol	M.P.C	% Yield	Color	R_f Value	Analysis (%), Found (calculated)		
							C	H	N
B_1	$C_{23}H_{21}NO_3S$	391	181	70	Yellow	0.83	70.58 (71.64)	5.37 (5.41)	3.58 (3.62)
B_2	$C_{24}H_{23}NO_3S$	405	184	62	Yellow	0.87	71.11 (71.18)	5.67 (5.64)	3.45 (3.49)
B_3	$C_{25}H_{25}NO_3S$	419	180	68	Yellow	0.81	71.59 (71.66)	5.96 (6.00)	3.34 (3.37)
B_4	$C_{26}H_{27}NO_3S$	433	178	65	Yellow	0.84	72.05 (72.09)	6.23 (6.27)	3.23 (3.26)
B_5	$C_{27}H_{29}NO_3S$	447	174	78	Yellow	0.81	72.48 (72.54)	6.48 (6.53)	3.13 (3.18)
B_6	$C_{28}H_{31}NO_3S$	461	170	75	Yellow	0.85	72.88 (72.93)	6.72 (6.74)	3.03 (3.05)
B_7	$C_{29}H_{33}NO_3S$	475	162	75	Yellow	0.88	73.26 (73.32)	6.94 (6.99)	2.94 (3.00)
B_8	$C_{30}H_{35}NO_3S$	489	156	79	Yellow	0.83	73.61 (73.64)	7.15 (7.21)	2.86 (2.89)
B_{10}	$C_{32}H_{39}NO_3S$	517	148	76	Yellow	0.91	74.18 (74.33)	7.43 (7.64)	2.70 (2.80)
B_{12}	$C_{34}H_{43}NO_3S$	545	129	72	Yellow	0.82	74.86 (74.90)	7.88 (7.95)	2.56 (2.63)
B_{14}	$C_{36}H_{47}NO_3S$	573	112	75	Yellow	0.83	75.39 (75.43)	8.20 (8.24)	2.44 (2.47)
B_{16}	$C_{38}H_{51}NO_3S$	601	110	76	Yellow	0.83	75.87 (75.80)	8.48 (8.53)	2.32 (2.36)
B_{18}	$C_{40}H_{55}NO_3S$	629	108	78	Yellow	0.86	76.31 (76.38)	8.74 (8.78)	2.22 (2.24)

on silica gel (80–120 mesh) using mixture of ethyl acetate/petroleum ether [7/3] followed by repeated recrystallization from ethanol. Melting point and other thermal properties of all the compounds (C_1 to C_8, C_{10} to C_{18}) are given in Table 2.

Analytical Data for a Few Respective Compounds

Series: II-Me [B-14] Molecular Formula: $C_{36}H_{47}NO_3S$ (573). **Elemental analysis** for calculated for C 75.43%, H 8.24%, N 2.47%; found C 75.39%, H 8.20%, and N 2.44%; **FT-IR (KBr pellet)**: 3091 cm^{-1} (-C-H Aromatic), 2973, 2880 cm^{-1} (-CH_3 CH_2, asymmetric ν_{as} and symmetric ν_s stretching, respectively), 1731 cm^{-1} (C=O group of cinnamate linkage), 1635 cm^{-1} (C=N stretching of Schiff base linkage), 1502 cm^{-1} (C=C stretching aromatic ring) **^{1}H-NMR ($CDCl_3$)**: 0.87–0.88 ppm (t, 3 H, CH_3 of aliphatic chain), 1.25–1.78 ppm (m, (-CH_2)n- of alkoxy chain), 2.17 ppm (s, 3H, -CH_3 of acetophenone), 4.03–4.07 ppm (t, 2 H, -OCH_2 of alkoxy chain), 6.40 and 7.96 ppm (d, 2 H, -CH=CH- of cinamate), **FAB mass spectra:** Molecular ion peak = 573(m/z = M^+).

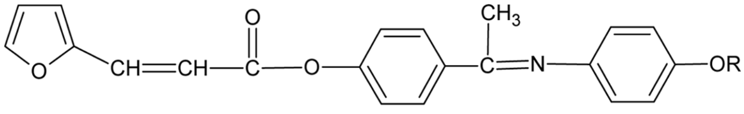
3. Results and Discussion

Mesomorphic properties and thermal stability for the two new homologous Series: I-Me and Series: II-Me were determined by hot stage polarizing microscopy and

Table 3. Transition temperature data of 4(furylacryloyloxy) α-methyl benzylidene-4′-*n*-alkoxyaniline (Series I-Me)

		Transitiontemperature in °C	
Code no.	R = *n*-alkyl	N	I
A_1	Methyl	127	210
A_2	Ethyl	123	214
A_3	Propyl	115	196
A_4	Butyl	120	202
A_5	Pentyl	108	173
A_6	Hexyl	110	186
A_7	Heptyl	104	160
A_8	Octyl	98	148
A_{10}	Decyl	79*	114
A_{12}	Dodecyl	96	109
A_{14}	Tetradecyl	70	107
A_{16}	Hexadecyl	69	106
A_{18}	Octadecyl	68	103

*Monotropic phase

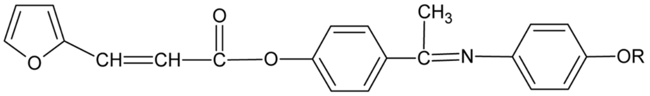


(Series I-Me)

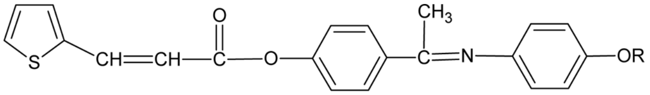
DSC and are given in Tables 3 and 4. The transition temperature data for the analogues compound of both the series are included for comparison in Tables 5 to 8. Data for the analogous compounds of both series are included for comparison. All the compounds show mesomorphic behavior.

In Series: I-Me, methoxy to octadecyloxy derivatives exhibit only nematic mesophase. No smectic mesophase is observed even in higher homologues. It is consistent with the assignment of each mesophase type, using the classification systems reported by Sackmann and Demus [35], Gray and Goodby [36]. The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (Fig. 4) exhibits usual odd–even effect and as the series is ascended the curve shows falling tendency.

In Series: II-Me, methoxy to octadecyloxy derivatives exhibit only nematic phase as in Series: I-Me, no smectic mesophase is observed. The plot of transition temperatures versus the number of carbon atoms in the alkoxy chain (Fig. 5) does not exhibit old–even effect as that of in Series: I-Me.



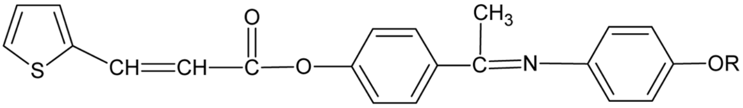
Series I-Me



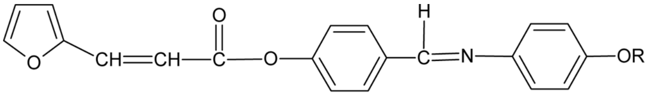
Series II-Me

Table 4. Transition temperature data of 4(thienylacryloyloxy) α-methyl benzylidene-4′-*n*-alkoxyaniline (Series II-Me)

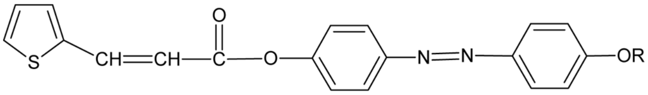
		Transition temperature in °C	
Code no.	R = n-alkyl	N	I
B_1	Methyl	137	181
B_2	Ethyl	141	184
B_3	Propyl	133	180
B_4	Butyl	135	178
B_5	Pentyl	130	174
B_6	Hexyl	129	170
B_7	Heptyl	127	162
B_8	Octyl	126	156
B_{10}	Decyl	131	148
B_{12}	Dodecyl	103	129
B_{14}	Tetradecyl	80	112
B_{16}	Hexadecyl	80	110
B_{18}	Octadecyl	78	108



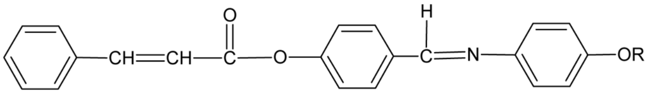
(Series II-Me)



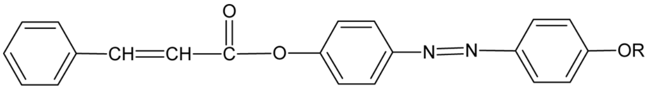
Series I-H [38]



Series II [39]



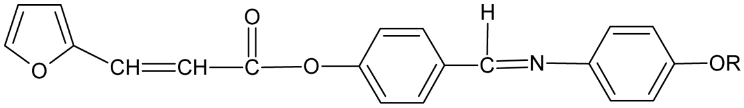
Series III-H [38]



Series- IV [39]

Table 5. Transition temperature data of 4(furylacryloyloxy) benzylidene-4′-*n*-alkoxyaniline (Series I-H) [38]

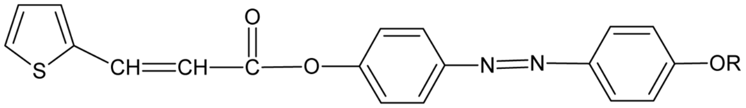
		Transition temperature in °C	
Code no.	R = *n*-alkyl	N	I
I_1	Methyl	138	220
I_2	Ethyl	128	226
I_3	Propyl	117	205
I_4	Butyl	122.5	207
I_5	Pentyl	110	191
I_6	Hexyl	117.5	196
I_7	Heptyl	94	180
I_8	Octyl	103	177
I_{10}	Decyl	98	171
I_{12}	Dodecyl	98.5	162
I_{14}	Tetradecyl	98	153
I_{16}	Hexadecyl	95	145



(Series I-H)

Table 6. Transition temperature data of 3-(thiophine-2-yl)-acrylic acid 4-(4-*n*-alkoxyphenylazo) phenyl ester (Series II) [39]

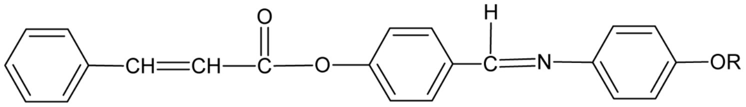
		Transition temperature in °C	
Code no.	R = *n*-alkyl	N	I
II_1	Methyl	161.7	235.7
II_2	Ethyl	178.2	235.1
II_3	Propyl	150.3	216.3
II_4	Butyl	159.2	215.7
II_5	Pentyl	133.5	201.4
II_6	Hexyl	136	197.8
II_7	Heptyl	124.3	187.1
II_8	Octyl	118.7	183.7
II_9	Nonyl	130.3	176.1
II_{10}	Decyl	112.3	172.4



(Series II)

Table 7. Transition temperature data of 4(cinnamoyloyloxy) benzylidene-4′-*n*-alkoxyaniline (Series III-H) [38]

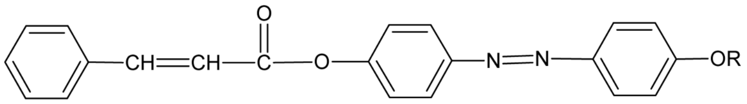
		Transition temperature in °C	
Code no.	R = *n*-alkyl	N	I
III_1	Methyl	131.5	226
III_2	Ethyl	155	234
III_3	Propyl	130	219
III_4	Butyl	128	216
III_5	Pentyl	118	207
III_6	Hexyl	114	201
III_7	Heptyl	108	198
III_8	Octyl	107	192
III_{10}	Decyl	106	179
III_{12}	Dodecyl	109	178
III_{14}	Tetradecyl	109	166
III_{16}	Hexadecyl	103	160



(Series III-H)

Table 8. Transition temperature data of 4-(4-*n*-alkoxyphenylazo) phenyl cinnamates (Series IV) [39]

		Transition temperature in °C	
Code no.	R = *n*-alkyl	N	I
IV_1	Methyl	146.5	242.4
IV_2	Ethyl	161.7	246.5
IV_3	Propyl	140.5	225.7
IV_4	Butyl	139.5	223.5
IV_5	Pentyl	121.8	209.0
IV_6	Hexyl	118.9	204.9
IV_7	Heptyl	117.3	195.0
IV_8	Octyl	118.3	190.8
IV_9	Nonyl	117.2	194.0
IV_{10}	Decyl	116.3	189.0



(Series IV)

Table 9. Average nematic thermal stability

Series	I-Me	II-Me	I-H	II	III-H	IV
Nimatic thermal stability	156.0 C_1-C_{18} 178 C_1-C_{10}	153.23 C_1-C_{18} 170 C_1-C_{10}	186.0 C_1-C_{16}	202.13 C_1-C_{10}	198.0 C_1-C_{16} 208 C_1-C_{10}	212 C_1-C_{10}

Table 10. Transition temperature and DSC data of the Series: I-Me and Series: II-Me

Compound code no.	Transition	Peak temp. (microscopic temp.) °C	ΔH (Jg^{-1})	ΔS ($jg\text{-}1k^{-1}$)
A_{10}	Cr-N	78.52 (79)	32.97	0.419
	N-I	114.70 (115)	109.61	0.955
A_{14}	Cr-N	70.57 (72)	27.16	0.388
	N-I	107.49 (108)	78.81	0.733
B_{10}	Cr-N	131.34 (130)	101.06	0.769
	N-I	149.11 (148)	120.42	0.804
B_{14}	Cr-N	80.24 (82)	24.68	0.307
	N-I	112.48 (112)	55.37	2.031

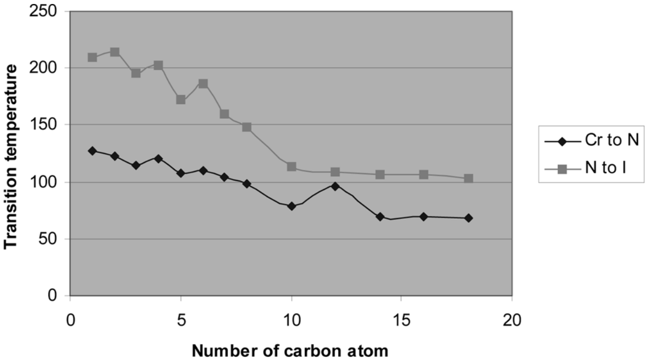


Figure 1. Transition temperature curve of Series: I-Me.

Comparison of molecules of Series: I-Me and Series: II-Me shows that they differ by terminal five membered heterocycle, which is oxo heterocycle in Series: I-Me and thio heterocycle in Series: II-Me. The average nematic thermal satiability of both the series is almost same. This indicates that α-methyl group which has created steric hindrance and by that way increased the breadth of the molecules over comes the negative effect created by the heterocyclic terminal linkage.

Molecules of Series: I-Me and Series: I-H differ only in an α-methyl group. On the Schiff base linkage present in Series: I-Me, rest of the molecules are same. It is known that α-methyl group increases the breadth of the molecules due to steric interaction and affects close packing of the molecules in nematic phase resulting into decrees in nematic thermal satiability of the molecules. Due to this reason, the average nematic thermal satiability of Series: I-Me is lower then those of Series: I-H (Table 9).

The molecules of Series: II-Me and Series: II differ by Schiff base linkage having α-methyl group and azolinkage in case of Series: II at that place. As discussed earlier α-methyl group of Schiff base linkage increase breadth of the molecules due to steric hindrance which reduces the nematic thermal satiability of Series: II-Me. This is the case (Table 9) average nematic thermal satiability of Series: II-Me is quite lower

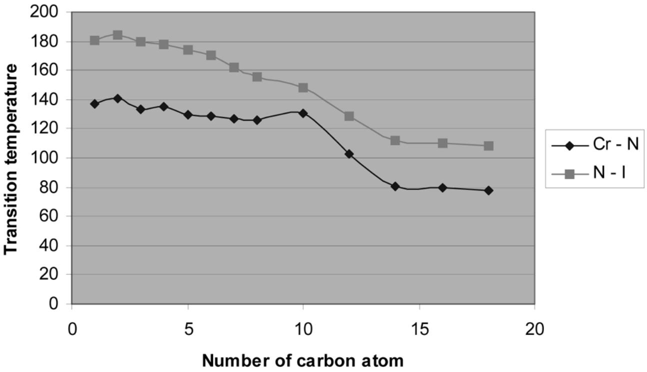


Figure 2. Transition temperature curve of Series: II-Me.

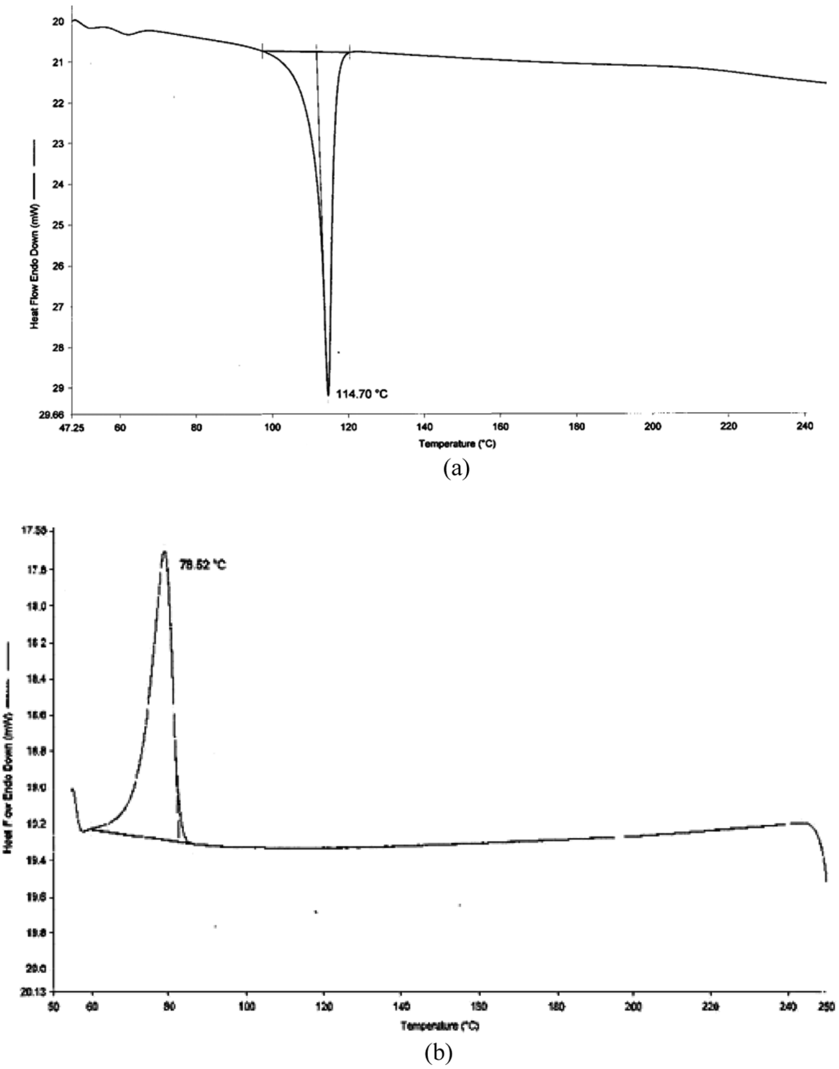


Figure 3. (a) DSC thermogram for compound A_{10} on heating (Series: I-Me). (b) DSC thermogram for compound no A_{10} on cooling (Series: I-Me).

compared to Series: II. The DSC data of few representative compounds of Series-I-MeA_{10} and A_{14} and Series-II-Me-B_{10} and B_{14} are given in Table 10 and their thermogram are shown in Figures 3 to 5. The transition temperature data obtained from OPM are almost agree with DSC thermogram peak data. Slightly vary in both temperature because of rate of changes of temperature are different in both the processes.

Influence of altering the nature and position of left hand heterocyclic ring by phenyl ring and α-methyl group on Schiff base linkage on mesomorphism: Molecules of Series: I-Me have oxoheterocyclic ring where as molecules of Series: III-H have phenyl ring at the end. Molecules of Series: I-Me have α-methyl Schiff base linkage as one of the center linkage where as molecules of Series: III-H have azomethyne linkage at that end.

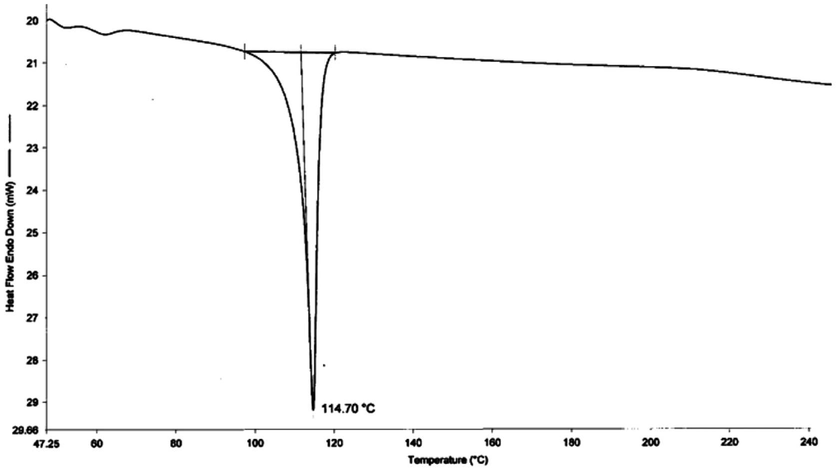


Figure 4. DSC thermogram for compound A_{14} (Series: I-Me).

Comparison of C_1-C_{10} member nematic thermal satiability of the Series: III-H is higher than Series: I-Me. This indicates the presence of oxoheteroatom cannot compensate the loss in molecular attractions created by α-methyl group in comparision to Series: III-H having classical calamitic molecular architecture.

The nematic thermal satiability of Series IV are slightly higher then those of Series: I-Me. This indicates that azolinkage of Series IV has played a batter role due to their polarizability in this series.

The nematic thermal satiability of Series: III-H and Series IV is higher then that of Series: II-Me. This may be related in the effect of linearity, polarizability, and subsequent packing of the molecule in the heterocyclic compounds.

Oh [37] has reported that all the transition temperature of pyridine analogous were lower compared with the benzene analogues.

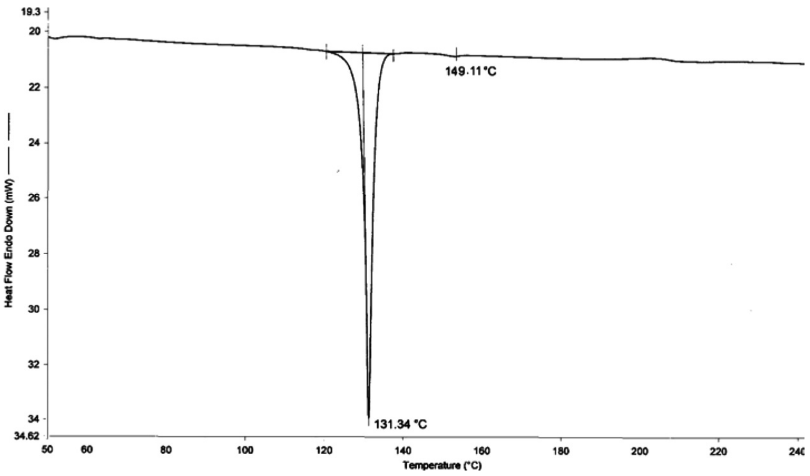


Figure 5. (a) DSC thermogram for compound B_{10} (Series: II-Me). (b) DSC thermogram for compound B_{14} (Series: II-Me).

In the present study, also the thiophene derivatives have lower transition temperature. The heteroatom has high electronegativity and will, therefore, withdraw electron from the other atoms of the ring system rendering the ring deactivated related to benzene.

4. Conclusion

A host of new compounds have been synthesized where one of the terminus is heterocyclic ring. α-Methyl group is introduced on one of the central Schiff base linkage. The terminal heterocycle ring is furan and thiophene. The study has highlighted that small differences in the molecular structure have a marked effect on mesophase thermal stabilities.

Acknowledgment

We are grateful to Prof. R. A. Vora retired Prof. and Head, Department of Applied Chemistry, Faculty of Technology and Engineering, Kalabhavan, M. S. University of Baroda, Vadodara for his valuable suggestion. We are also thankful to CDRI Lucknow, I.I.T. Bombay, and SAIF Chandighar for providing facilities of elemental analysis, FT-IR, ^{1}H-NMR, mass spectral, and thermal analysis.

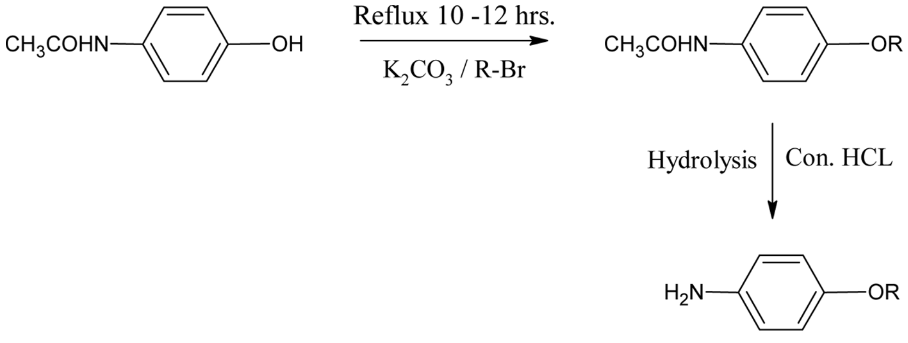
References

[1] Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystals*, Academic Press: New York.
[2] Lin, H. C., Lai, L. L., Hsieh, W. P., & Huang, W. Y. (1997). *Liq. Cryst.*, *22*, 661.
[3] Semmler, K. J. K., Dingemans, T. J., & Samulski, E. T. (1998). *Liq. Cryst.*, *24*(6), 799.
[4] Tokuhisa, H., Era, M., & Tsutsui, T. (1998). *Appl. Phys. Lett.*, *72*, 2639.
[5] Tokuhisa, H., Era, M., & Tsutsui, T. (1998). *Adv. Mater.*, *10*, 404.
[6] Sato, M., Ohta, R., Handa, M., & Kasuga, K. (2002). *Liq. Cryst.*, *29*, 1441.
[7] Karamysheva, L. A., Torgova, S. I., & Agafonova, I. F. (2000). *Liq. Cryst.*, *27*, 393.
[8] Cai, R., & Samulski, E. T. (1991). *Liq. Cryst.*, *9*, 617.
[9] Parra, M., Alderete, J., Zuniga, C., Hidalgo, P., Vergara, J., & Fuentes, G. (2002). *Liq. Cryst.*, *29*, 1375.
[10] Hsu, Y. Y. (1984). U.S. Patent 4 424 372.
[11] Schadt, M. (1993). *Liq. Cryst.*, *14*, 73.
[12] Demus, D. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 25.
[13] Gray, G. W., & Kelly, S. M. (1999). *J. Mater. Chem.*, *9*, 2037.
[14] Bretle, R., Dunmur, D. A., Marson, C. M., Pinol, M., & Toriyama, K. (1993). *Liq. Cryst.*, *13*, 515.
[15] Bretle, R., Dunmur, D. A., Marson, C. M., Pinol, M., & Toriyama, K. (1992). *Chem. Lett.*, *21*, 613.
[16] Seed, Alexander. (2007). *Chem. Soc. Rev.*, *36*, 2046–2069.
[17] Press, J. B. (1984). In: *The Chemistry of Heterocyclic Derivatives. Thiophene and its Derivatives*; Gronowitz, S. (Ed.), Wiley: New York, Vol. 44 (Part-1), 353–456.
[18] Press, J. B. (1990). In: *The Chemistry of Heterocyclic Derivatives. Thiophene and its Derivatives*; Gronowitz, S. (Ed.), Wiley: New York, Vol. 44 (Part-4), 397–502.
[19] Fishel, D. L., & Patel, P. R. (1972). *Mol. Cryst. Liq. Cryst.*, *17*, 139.
[20] Nash, J. A., & Gray, G. W. (1974). *Mol. Cryst. Liq. Cryst.*, *25*, 299.
[21] Pavluchenko, A. I., Smirnova, N. I., Titov, V. V., Kovshev, E. I., & Djumeev, K. M. (1976). *Mol. Cryst. Liq. Cryst.*, *37*, 35.

[22] Dewar, M. J. S., & Riddle, R. M. (1975). *J. Amer. Chem. Soc.*, *97*, 6658.
[23] Thaker, N. N., & Trivedi, K. N. (1981). *Indian J. Chem.*, *20A*, 560.
[24] Nguyen, D. N., & Pham, T. C. (1976). *Tap. Chi. Hoa. Hoc.*, *14*, 13.
[25] Dave, J. S., & Lohar, J. M. (1981). *Mol. Cryst. Liq. Cryst.*, *70*, 279.
[26] Jones, F. Jr., & Ratto, J. (1973). *J. Chem. Soc., Chem. Commun.*, *21*, 841.
[27] Agrawal, Y. K., & Rajput, S. J. (1997). *J. Indian Chem. Soc.*, *74*, 689.
[28] Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., & Vill, V. (Eds.). (1998). *Handbook of Liquid Crystals*, VCH-Wiley: Weinheim.
[29] Saleh, A. A., Pleune, B., Fettinger, J. C., & Poli, R. (1997). *Polyhedron*, *16*, 1391.
[30] Vyas, G. N., & Shah, N. M. (1963). *Org. Syn. Coll.*, John Wiley and Sons Inc.: New York, Vol. IV, 836.
[31] Criswell, T. R., Klanderman, B. H., & Batesky, B. C. (1973). *Mol. Cryst. Liq. Cryst.*, *22*, 211.
[32] Vora, R. A., & Dixit, N. (1979). Presented at Annual Convention of Chemists, Kurukshetra, India.
[33] Vogel, A. I. (1972). In: *Textbook of Practical Organic Chemistry*, 3rd Edition, (E. L. B. S. and Longman Group Ltd., London, 251.
[34] Dave, J. S., & Vora, R. A. (1970). Mesomorphic behavior of the cholestryl esters-1. Pera normal alkoxy benzoates of cholesterol. In: *Liquid Crystals and Ordered Fluid*, Johnson, J. F. & Porter, R. S., (Eds.), Plenum Press: New York, 1, 477.
[35] Sackmann, H., & Demus, D. (1966). *Mol. Cryst. Liq. Cryst.*, *2*, 81.
[36] Gray, G. W., & Goodby, J. (1984). *Smectic Liquid Crystals: Textures and Structures*. Leonard Hill, Glasgow.
[37] Oh, C. S. (1972). *Mol. Cryst. Liq. Cryst.*, *19*, 95.
[38] Vora, R. A., & Gupta, Renu. (1983). *Mol. Cryst. Liq. Cryst.*, *91*, 45–52.
[39] Matharu, A. S., & Chambers-asman, D. (2007). *Liq. Cryst.*, *34*(11), 1317–1336.

Scheme 1 (Series: I-Me)

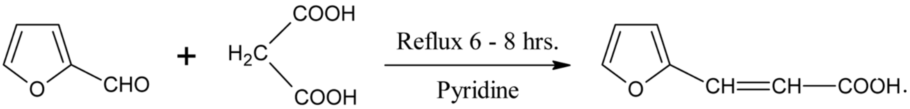
Synthesis of 4-n-alkoxy anilines



[A]

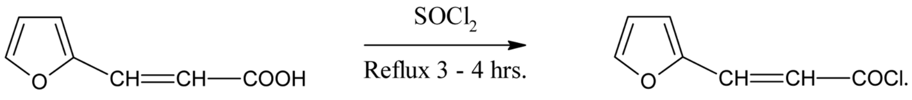
where C_nH_{2n+1} n = 1 to 8, 10, 12, 14, 16, and 18.

Synthesis of furylacryoyl acid



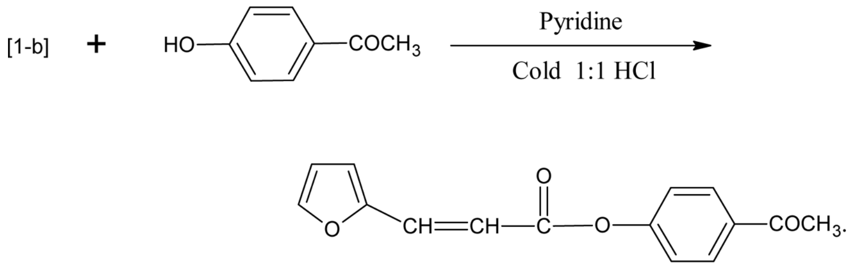
[1-a]

Synthesis of furylacryoyloxy chloride



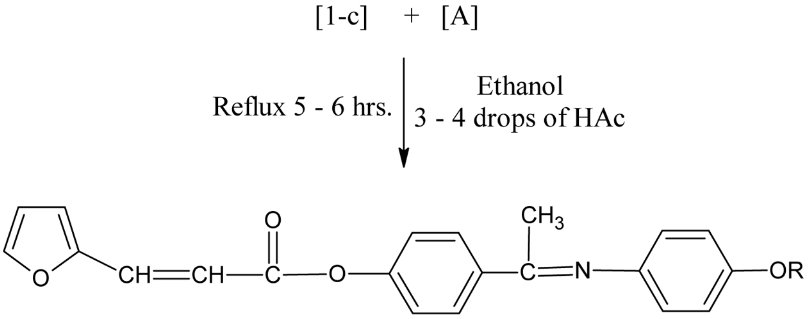
[1-b]

Synthesis of 4(furylacryloyloxy) acetophenone



[1-c]

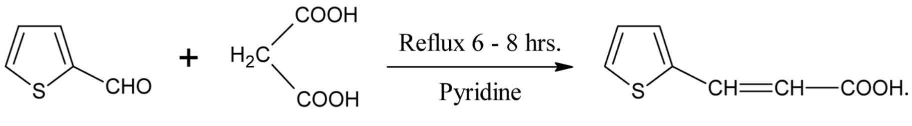
Synthesis of 4(furylacryloyloxy) α-methyl benzylidene-4′-n-alkoxyaniline



Series: I-Me

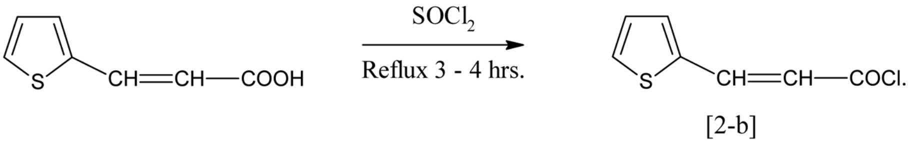
where C_nH_{2n+1} n = 1 to 8, 10, 12, 14, 16, and 18.

Scheme 2 (Series: II-Me)
Synthesis of thionylacrylic acid

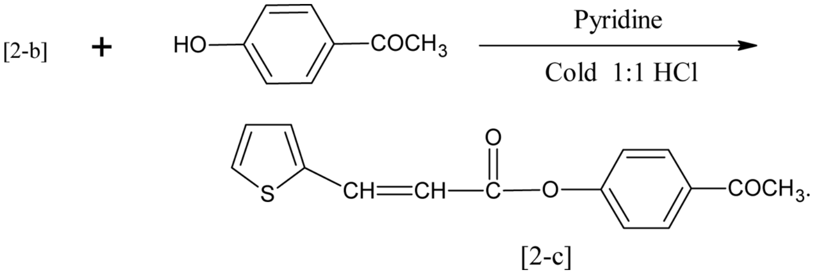


[2-a]

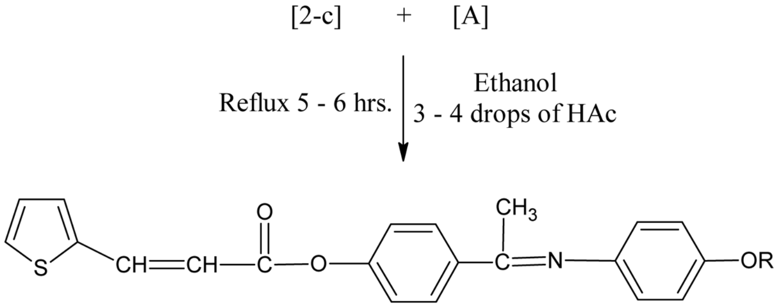
Synthesis of thionylacryloyl chloride



Synthesis of 4(thionylacryloyloxy) acetophenone



Synthesis of 4(thionylacryloyloxy) α-methyl benzylidene-4′-n-alkoxyaniline



Series: II-Me

where C_nH_{2n+1} n = 1 to 8, 10, 12, 14, 16, and 18.