



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

### Synthesis, Characterization, and Mesogenic Properties of Anisotropic Imines

Krishna C. Majumdar<sup>a</sup>, Nilasish Pal<sup>a</sup>, Sanjay Nath<sup>a</sup>,  
Sudip Choudhury<sup>b</sup> & Nandiraju V. S. Rao<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Kalyani,  
Kalyani, West Bengal, India

<sup>b</sup> Department of Chemistry, Assam University,  
Silchar, Assam, India

Version of record first published: 31 Jan 2007

To cite this article: Krishna C. Majumdar, Nilasish Pal, Sanjay Nath, Sudip Choudhury & Nandiraju V. S. Rao (2006): Synthesis, Characterization, and Mesogenic Properties of Anisotropic Imines, *Molecular Crystals and Liquid Crystals*, 461:1, 37-51

To link to this article: <http://dx.doi.org/10.1080/15421400600983531>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to

date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Synthesis, Characterization, and Mesogenic Properties of Anisotropic Imines

**Krishna C. Majumdar**

**Nilasish Pal**

**Sanjay Nath**

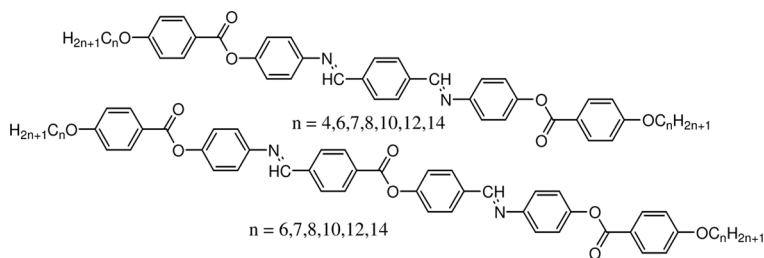
Department of Chemistry, University of Kalyani,  
 Kalyani, West Bengal, India

**Sudip Choudhury**

**Nandiraju V. S. Rao**

Department of Chemistry, Assam University, Silchar, Assam, India

*Two homologous series of highly anisotropic diimines containing five and six aromatic rings in the mesogenic core derived from 1,4-terephthaldehyde and 4-formylphenyl-4-formylbenzoate have been synthesized and characterized by spectroscopic methods. The liquid-crystalline phases and the phase-transition temperatures are investigated using a polarizing microscope attached to a hot stage and differential scanning calorimetry. Most of the compounds are thermally stable and exhibit smectic and nematic phases over a large thermal range. In the majority of the compounds studied, a SmC phase exists over a very broad temperature range. The importance of the alkyl chain length in competing with the size of the aromatic core in determining the phase variant and in the increase of thermal range of the mesomorphism in a homologous series is described.*

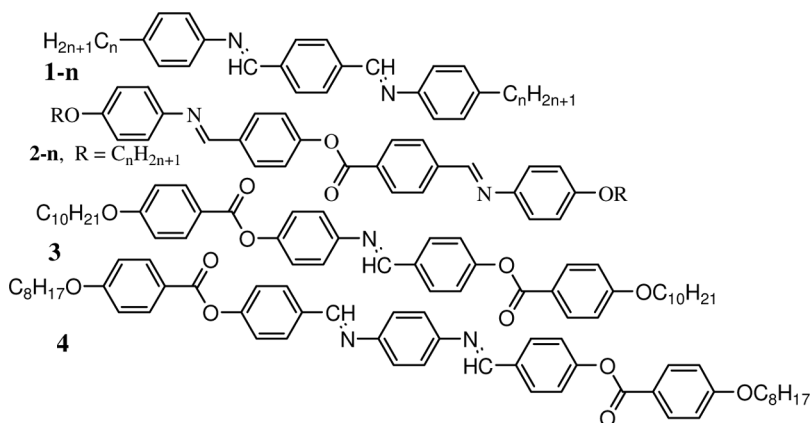


**Keywords:** alkyl chain length; imines; schiff's bases; smectic polymorphism

Address correspondence to Nandiraju V. S. Rao, Department of Chemistry, Assam University, Silchar, Assam 788 011, India. E-mail: nvsrao@sancharnet.in or Krishna C. Majumdar, Department of Chemistry, University of Kalyani, Kalyani, Nadia-741235, India. E-mail: kcm\_ku@yahoo.co.in

## INTRODUCTION

The discovery of room-temperature liquid crystal *N*-(4-methoxybenzylidene)-4'-*n*-butylaniline, popularly known as MBBA [1], followed by 4-cyanobiphenyls [2] containing two unsaturated phenyl rings with terminal substituents motivated several scientists to synthesize new materials, extending the terminal substituents either by aromatic or aliphatic rings and/or branched chains or multiple substituents exhibiting mesogenic properties. In the past three decades, many typical examples of compounds have been reported that exhibit liquid-crystalline behavior, possessing an imine, ester, thioester, azo, tolane, or biphenyl linkage linking two or more phenyl rings with identical or different substituents at the ends. The substituent at one end is an aliphatic chain, while the other end is substituted with the same or a different alkyl chain or any other polar or nonpolar groups. The phase variants in these materials also depend on the linking groups, number of aromatic rings promoting conjugation, and also the end substituent, which may be chiral or achiral alkyl groups or polar or nonpolar functional groups. Further the **nOm** homologues, *viz.* *N*-(4-*n*-alkoxybenzylidene)alkylanilines (two-ring system) [3] and TBnA homologues terephthalylidene-bis-4-*n*-alkylanilines (three ring system) [4], are particularly interesting because they exhibit unusually broad polymorphism exhibiting nematic, A, C, I, F, B, crystal G, H phases. In recent years, the study of low-molar-mass mesogens consisting of a Schiff base as well as ester linkages with a three-ring system possessing imine linkage **1-n** [4], four ring **2-n** and **3** [5], and five ring **4** [5] systems comprising imine as well as ester linkages have been well documented wherein the length of end alkyl chain influences the liquid-crystalline properties. Further, the metal complexation of the compounds increases the rigidity with increasing or decreasing thermal stability depending upon the metal. Owing to the interest in the tilted smectic phases and to study the influence of the length of the aromatic moiety in the rigid core with respect to the length of aliphatic chains related to mesomorphic properties, we synthesized five-ring **5-n** and six-ring **6-n** systems with a variation in chain length. In this article, we report the synthesis and characterization of some compounds of two homologues series terephthalylidenebis-4-(4'-*n*-alkyloxybenzoyloxy)aniline **5-n** and 4[4'-((4''-*n*-alkoxybenzoyloxy)phenyliminomethylphenyl)-4-(4'-(4''-*n*-alkoxybenzoyloxy)phenyliminomethylphenyl) benzoate] **6-n**:



Compound **1-n**: terephthalaldehyde-bis-(4-n-alkylanilines).

Compound **2-n**: (4-n-decyloxybenzoyloxyphenyliminomethylphenyl)-4-N-(4-n-decyloxyphenyliminomethyl-benzoate).

Compound **3-n**: *N*-(4-n-decyloxybenzoyloxy-4'-benzylidene)-4''-decyloxybenzoyloxy-4'''-aniline, [5].

Cr 104 (enthalpy 17.5 kJ/mol, entropy 46 JK<sup>-1</sup> mol<sup>-1</sup>) *J* 117 (23.1, 60)

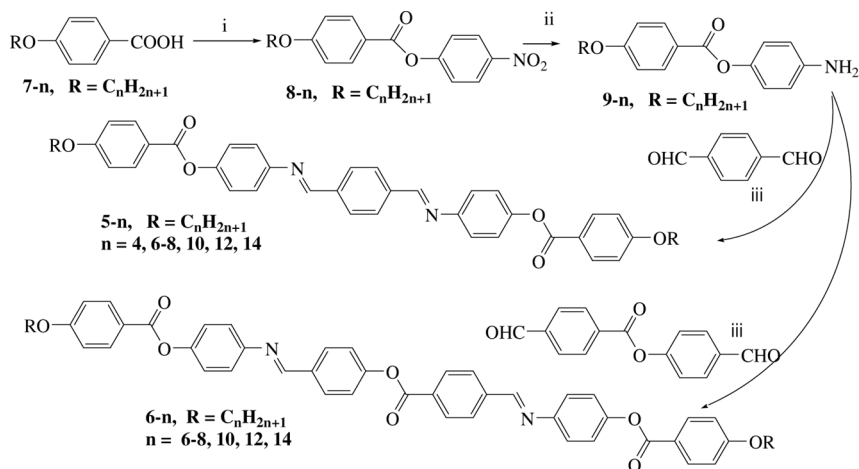
Sm I 129 (1.0, 2) Sm C 232 (3.1, 6) N 288 (1.9, 3)I.

Compound **4**: *N,N'*-bis-[4-((4-n-decyloxybenzoyloxy)benzylidene)phenylene-1,4-diimine] [6].

Cr 88°C Cr1 117°C Cr2 144°C SmJ 151°C SmI 167°C SmC 172°C SmC' 290°C N 422°C I.

## SYNTHESIS OF THE COMPOUNDS

The synthetic routes of the compounds synthesized are presented in Scheme 1. 4-n-Alkoxybenzoic acids were obtained via Williamson ether reaction between the relevant 1-bromoalkane and ethyl-4-hydroxybenzoate followed by hydrolysis of the ethyl-4-n-alkoxybenzoate. 4-n-Alkoxybenzoyloxy-4'-nitrobenzene was then obtained by the esterification of 4-n-alkoxybenzoic acid chloride with 4-nitrophenol by phase-transfer catalysis. The corresponding amines were obtained by subsequent reduction of the nitro compound using 10% Pd-C. 4-Formylphenyl-4-formylbenzoate was obtained by classical *N,N'*-dicyclohexylcarbodiimide (DCC)-4-(*N,N*-dimethylamino) pyridine (DMAP) (DCC-DMAP) method of esterification of 4-formylbenzoic acid with 4-hydroxybenzaldehyde. The 4-n-alkoxybenzoyloxy-4'-aminobenzene was then condensed either with terephthalaldehyde or 4-formylphenyl-4-formylbenzoate in absolute ethanol in the presence of glacial acetic



**SCHEME 1** Reagents and conditions: i) a.  $SOCl_2$ , reflux, 1 h; b. *p*-nitrophenol,  $CH_2Cl_2$ , aq.  $K_2CO_3$ ,  $Bu_4NHSO_4$ , r.t., 12 h; ii)  $H_2$  10% Pd/C (Cat.), EtOAc, r.t., 12 h; iii) abs. EtOAc, cat. AcOH, reflux, 1 h.

acid to give the target imines, **5-n** and **6-n**. The new homologues of **5-n** and **6-n** presented here were characterized by spectroscopic methods ( $^1H$  NMR, IR) and elemental analysis. The molecular structures are in full agreement with the formulae and spectroscopic data. The experimental elemental values are found to be in good agreement with the estimated C, H, and N composition.

## RESULTS AND DISCUSSION

### Mesomorphism of the Compounds

The phase-transition temperatures, associated enthalpies, corresponding entropies, and the observed phases detected by differential scanning calorimetry (DSC) and thermal microscopy are presented in Table 1. The compounds synthesized in this work consists of either five or six aromatic rings and are different from the earlier reported compounds of three-ring or four-ring systems, *viz.* terephthalylidene-bis-4-*n*-alkylanilines, 4-*N*-(4-*n*-decyloxybenzoyloxy-4'-benzylidene)-4''-decyloxybenzoyloxy-4'''-aniline, *N,N'*-bis-[4-(4-*n*-decyloxybenzoyloxy)benzylidene]phenylene-1,4-diimine, by an increase in significant anisotropy of polarizability due to extended conjugation.

The lower homologues **5-n** of terephthaldehyde derivatives and **6-6** and **6-7** of 4-formylphenyl-4'-formylbenzoate derivatives exhibit phase

**TABLE 1** Transition Temperatures, Associated Enthalpies, and Entropies of the Phase Transitions of the Compounds **5-n**, **n = 4, 6, 7, 8, 10, 12, and 14** and **6-n**, **n = 6, 7, 8, 10, 12, and 14**

Compound	Transition	T/°C	$\Delta H/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S/\text{JK}^{-1} \cdot \text{mol}^{-1}$
<b>5-4</b>	Cr-Cr1	144.6	0.06	0.02
	Cr1-Cr2	146.6	0.47	1.12
	Cr2-I	157.1	3.19	7.42
	I-C	161.3	0.34	0.78
	C-N	197.3	0.06	0.12
	N-I	>350		
<b>5-6</b>	Cr-Cr1	63.3	0.79	2.37
	Cr1-J	146.3	2.65	6.33
	J-I	165.9	0.07	0.16
	I-C	169.4	0.15	0.34
	C-N	281.3	0.02	0.05
	N-I	>350		
<b>5-7</b>	Cr-Cr	66.7	0.26	0.59
	Cr-J	134.3	2.20	5.41
	J-I	161.5	0.04	0.09
	I-C	169.6	0.17	0.38
	C-N	303.4	0.11	0.19
	N-I	>350		
<b>5-8</b>	Cr-Cr	65.9	0.75	2.22
	Cr-Cr	107.6	4.45	11.7
	Cr-J	109.1	20.3	53.1
	J-I	156.9	0.26	0.62
	C-N	321.6	1.68	2.83
	N-I	>350		
<b>5-10</b>	Cr-Cr	86.6	8.12	22.5
	Cr-J	89.6	24.1	66.4
	J-I	136.9	0.03	0.08
	I-C	162.9	2.81	6.46
	C-N	327.4	2.98	4.97
	N-I	>350		
<b>5-12</b>	Cr-J	62.9	22.6	67.5
	J-I	145.1 <sup>a</sup>	—	—
	I-C	156.8	0.41	0.95
	C-A	295.6	1.60	2.82
	A-N	333.6	0.22	0.36
	N-I	>350		
<b>5-14</b>	Cr-J	71.1	19.9	57.8
	J-I	72.5	14.2	41.1
	I-C	142.2	1.49	3.58
	C-A	306.5	1.87	3.23
	A-N	344.6	0.01	0.01
	N-I			

(Continued)

TABLE 1 Continued

Compound	Transition	T/°C	$\Delta H/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S/\text{JK}^{-1} \cdot \text{mol}^{-1}$
<b>6-6</b>	Cr-I	127.3	28.3	70.8
	I-C	147.6	0.54	1.30
	C-N	340.2	—	—
	N-I	>350	—	—
<b>6-7</b>	Cr-I	132.0	28.6	70.6
	I-C	176.3	3.25	7.23
	C-N	319.0	—	—
	N-I	>350	—	—
<b>6-8</b>	Cr-J	118.4	13.9	35.5
	J-I	152.3	1.02	2.40
	I-C	255.1	—	—
	C-N	292.1	—	—
	N-I	>350	—	—
<b>6-10</b>	Cr-J	119.0	16.3	41.6
	J-I	165.2	2.23	5.09
	I-C	209	—	—
	C-N	285	—	—
	N-I	>350	—	—
<b>6-12</b>	Cr-J	115.0	5.35	13.7
	J-I	117.7	2.64	6.76
	I-C	137.9	1.97	4.80
	C-A	242	—	—
	A-N	251	—	—
	N-I	>350	—	—
<b>6-14</b>	Cr-J			
	J-I	115.2	5.80	14.9
	I-C	142.4	1.23	2.96
	C-A	306.1	—	—
	A-N	328.1	—	—
	N-I	>370	—	—

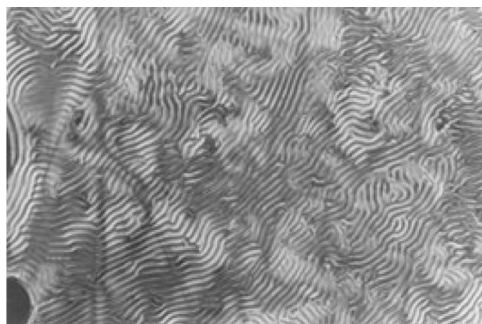
variant phase variant nematic, smectic C smectic I (NCI). However, the middle homologues, **5-6**, **5-7**, **5-8**, **5-10**, **6-8**, **6-10**, of both homologous series exhibit nematic, SmC, SmI, and SmJ phases. The higher homologues **5-12**, **5-14**, **6-12**, and **6-14** exhibit a SmA phase in addition to N, SmC, SmI and SmJ phases. However, neither the expected quenching of smectic phases (A or C) nor the direct appearance of a bond orientational ordered smectic I phase from isotropic phase has been observed as a result of the increase in flexible end alkyl chain length  $n=14$ , as expected in these compounds, and which was reported earlier in **nOm** compounds. This may be occurring because of the presence of the increased size of the rigid core manifesting as an enhanced longitudinal polarizability by way of four or five aromatic



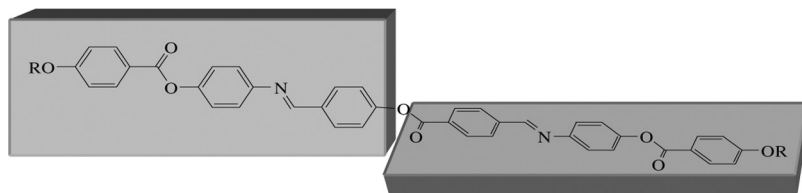
ring systems in comparison to the two-ring systems of the **nOm** series. Hence in these homologous compounds, the ratio of the flexible chain length to rigid core lengths is not sufficient even in higher homologues to quench the SmA or SmC phases to exhibit bond orientational ordered smectic I or smectic F phases directly from the isotropic phase [7]. Further, the appearance of the SmA phase started only in compounds of both homologous series **5-n** and **6-n**, when the carbon chain length is 12 ( $C_{12}H_{25}$ ) and above, *i.e.*, **5-12**, **5-14**, **6-12**, and **6-14**. This is an indication of the influence of the end alkyl chain length to promote orthogonal phases and their competition with lateral out-board dipolar forces of the molecules, which promote titled phases. All the compounds exhibit crystal-crystal phase transitions before transforming into a liquid-crystalline phase. Moreover the melting temperatures of the imine compounds as observed in DSC generally decrease with larger alkyl chain length ( $n = 8$  or more) with few exceptions. All the samples were not isotropic until  $350^{\circ}\text{C}$  and are highly fluid in nature. Prolonged heating at this temperature also did not give any indication of decomposition. The details of the observation of microscopic textures are presented for only two compounds, **5-7** (phase variant NCI) and **6-12** (phase variant NACIJ), as representative examples because other homologues exhibit similar phase variants.

### Chiral Nematic Phase

The common feature of the observed texture of the nematic phase in all the compounds is a characteristic fingerprint texture resembling chiral nematic phase as shown in Fig. 1 exhibited by the compound **5-12**. The texture of this nematic phase in homologues of **6-n** also



**FIGURE 1** Fingerprint texture of chiral nematic phase of **5-12** at  $349^{\circ}\text{C}$ .

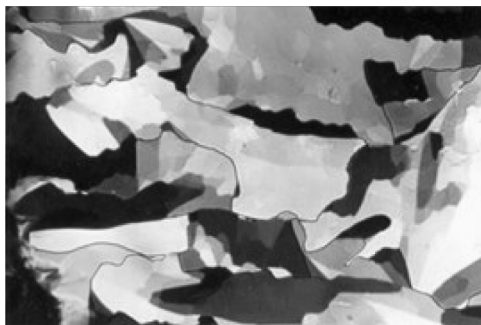


**FIGURE 2** Possible model of the molecule.

resembles the same texture but with little distortion. We believe that this texture may be result of the conformational chirality in the phenyl ester moieties induced as a result of the twist of two planes of aromatic moieties, as shown in Fig. 2, at the benzoate linkage similar to the observation reported recently by Kishikawa *et al.* [8]. The dipole–dipole intermolecular interaction between the ester linkages, in phenyl benzoate homologues, is important in the self-assembly of molecules with rotational freedom to promote chirality in the nematic phase. The sample is not viscous, and the texture disappears after shearing and reappears after some time.

### Phase Assignment, 5–7

All the phase transformations were observed by changes in optical textures using a polarizing microscope attached to a hot stage. The sample **5–7** in the heating cycle did not exhibit any characteristic textures for the identification of liquid-crystalline phases but the transitions were observed by way of change in texture transformation until 350°C. The experimental limitation did not allow going beyond 350°C but the sample **5–7** transformed into nematic phase at this temperature with the appearance of either marble or fingerprint texture in this temperature region of nematic phase. Sometimes a schlieren-like texture was also observed. On cooling, the sample exhibited a phase transition at 303.4°C with the appearance of schlieren texture from the marble texture characterizing the phase as a smectic C phase. The sample on further cooling exhibited a schlieren mosaic-like or platelet texture as shown in Fig. 3, with the disappearance of four brush schlieren texture at 169.6°C resembling the textures of the smectic I phase observed in **nOm** compounds [6]. However, this texture is found to be different from the textures of broken focal conic or platelet texture characteristic of smectic **F** phase exhibited by **nOm** compounds. The smectic I phase is found to be present in all the compounds. The phase on subsequent cooling transformed into a mosaic-like texture



**FIGURE 3** Platelet texture of smectic **I** phase of **5–7** at 163.5°C.

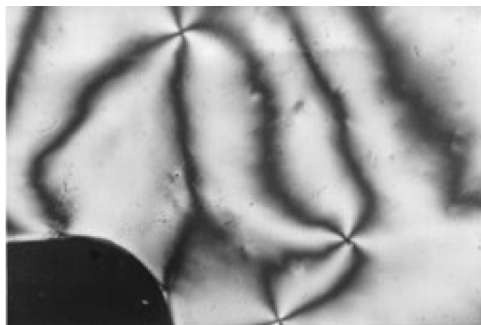
at 161.5°C as shown in Fig. 4, characterizing the phase as a smectic **J** phase. Further cooling of the sample transformed it into a solid phase at 134.3°C with the appearance of characteristic texture of solid phase. A comparison of the liquid-crystalline thermal range in the homologous series indicates the significant influence of alkyl chain length.

### Phase Assignment, **6–12**

All the compounds of the homologous series **6–n** ( $n = 6–10, 12$ , and  $14$ ) exhibit a nematic phase up to 350°C and greater, and hence the clearing temperatures could not be recorded. The compound **6–12** exhibits schlieren (Fig. 5) as well fingerprint texture of periodic stripes, with striation lines across the texture. Further cooling of the nematic phase reveals a SmA phase characterized by the focal conic fan texture (Fig. 6). On further cooling, it exhibited schlieren texture at 242°C, characterizing the phase as SmC (Fig. 7). The SmC phase range is



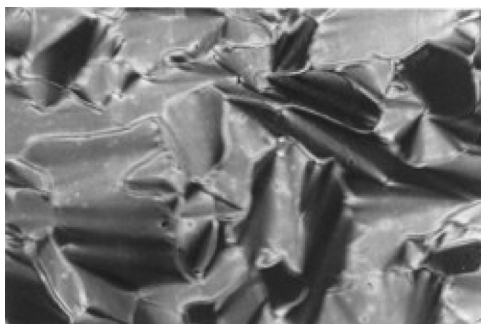
**FIGURE 4** Mosaic texture of smectic **J** phase of **5–7** at 150.2°C.



**FIGURE 5** Schlieren texture of nematic phase of **6-12** at 278.9°C.

very large in lower homologues, which decreases to a minimum of 37°C in **6-8** and once again increases with increasing chain length. The SmC phase transforms into a SmI phase with the appearance of mosaic-like or platelet textures at 137.9°C, which subsequently transformed into a mosaic-like texture characteristic of SmJ phase at 117.7°C before solidifying at 115°C to form a crystalline phase.

A comparison of thermal properties of the compounds **5-10**, **3**, and **4** revealed that the thermal stability increases with an increase in the number of phenyl rings of these compounds. In spite of the difference in number of phenyl rings (between **5-10** and **3**[5]), or the direction of imine linkage (between **5-10** and **4**[6]), all the three compounds exhibited the identical phase variant NCIJ. Similarly the homologues of **6-n** are found to exhibit the same phase variant NCI that was observed in compounds with reduced number of phenyl rings (**2-n**  $R = C_nH_{2n+1}$ ,  $n = 4, 8$ , and  $12$ ).



**FIGURE 6** Focal conic fan texture of smectic A phase of **6-12** at 247°C.



**FIGURE 7** Smectic C schlieren texture of **6-12** at 236°C.

Most of these compounds exhibit tilted phases. The lateral dipole moment of the molecules, which is at an angle with the molecular long axis, promotes tilted phases. The competition between and alkyl chains promoting orthogonal phases like SmA and SmB phases and the outboard dipole moment on the central rigid core, which promotes tilted phases, it apparent by the phase variant exhibited by these homologues series. Hence the observed orthogonal SmA phase in compounds of dodecyl (**5-12**, **6-12**) homologues and tetradecyl (**5-14** and **6-14**) homologues of both homologous series only when the alkyl chain length has been increased supports such hypothesis.

## EXPERIMENTAL

All the chemicals were procured from either Tokyo Kasei Kogyo Co. Ltd. or Spectrochem, India. Silica gel [60–120 mesh, Spectrochem, India] was used for chromatographic separation. Silica gel G [E-Merck, India] was used for thin-layer chromatography (TLC). Petroleum ether refers to the fraction boiling between 60°C and 80°C. The synthesis of 4'-formylphenyl-4-formylbenzoate was carried out by a well-documented procedure in the literature. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer ( $\nu_{\max}$  in  $\text{cm}^{-1}$ ) on KBr disks. UV absorption spectra were recorded in  $\text{CHCl}_3$  on a Shimadzu UV-2401PC spectrophotometer ( $\lambda_{\max}$  in nm).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (300 MHz, 500 MHz) spectra were recorded on Bruker DPX-300 and Bruker DPX-500 spectrometers in  $\text{CDCl}_3$  (chemical shift in  $\delta$ ) with TMS as internal standard. The liquid-crystalline properties were established by thermal microscopy (Nikon), and the phase transitions were confirmed by DSC (Perkin-Elmer DSC Pyris1 system).

### Synthesis of 4'-Nitrophenyl-4-hexyloxybenzoate 8

4-Hexyloxybenzoic acid (2 g, 9 mmol) and excess thionyl chloride (5 ml) were refluxed for 1 h and then the excess thionyl chloride was evaporated under reduced pressure. The resulting acyl chloride was dissolved in dichloromethane (30 ml) and 4-nitrophenol (1.25 g, 9 mmol), and then tetrabutylammonium hydrogensulphate (0.15 g, 0.45 mmol), potassium carbonate (1.86 g, 13.5 mmol), and water (15 ml) were added. The mixture was stirred vigorously for 12 h. The organic layer was separated, washed with water ( $2 \times 20$  ml) and dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent gave the crude product, which was then purified by column chromatography ( $\text{SiO}_2$ , eluent ethyl acetate–petroleum ether 95:5 v/v), and the solvent was evaporated to give pure compounds **8**. Yield 82%, UV  $\lambda_{\text{max}}$ : 206, 277 nm.

IR  $\nu_{\text{max}}$ : 1253, 1516, 1607( $\nu_{\text{C}=\text{C}}$ ), 1742( $\nu_{\text{C}=\text{O}}$ ), 2867, 2929( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.26 (d,  $J = 8.4$  Hz, 2H), 8.10 (d,  $J = 8.4$  Hz, 2H), 7.37 (d,  $J = 8.7$  Hz, 2H), 6.96 (d,  $J = 8.7$  Hz, 4H), 4.01(t,  $J = 6.6$  Hz, 2H), 1.84–0.88 (m, 11H).

### Synthesis of 4'-Aminophenyl-4-hexyloxybenzoate 9

Compound **2** was dissolved in ethyl acetate, and a catalytic amount of 10% Pd/C was added. The mixture was stirred at room temperature for 12 h in an atmosphere of hydrogen. It was then filtered, and the solvent was removed under reduced pressure to get the crude product, which was crystallized from ethanol to give the pure compound **9**. Yield 90%; UV  $\lambda_{\text{max}}$ : 209, 259 nm; IR  $\nu_{\text{max}}$ : 1258, m 1607( $\nu_{\text{C}=\text{C}}$ ), 1725( $\nu_{\text{C}=\text{O}}$ ), 2858, 2933( $\nu_{\text{CH}}$ ), 3406( $\nu_{\text{NH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  8.10 (d,  $J = 8.4$  Hz, 2H), 6.99–6.93 (m, 4H), 6.68 (d,  $J = 9.0$  Hz, 2H), 4.0 (t,  $J = 6.6$  Hz, 2H), 1.84–0.88 (m, 11H).

### General Procedure for the Preparation of 5-n and 6-n

An ethanolic (20 ml) solution of terephthalaldehyde or 4'-formylphenyl-4-formylbenzoate was added to an ethanolic solution of 4'-aminophenyl-4-alkoxybenzoate. The solution mixture was refluxed with few drops of glacial acetic acid as catalyst for 1 h to yield the yellowish Schiff's base. The precipitate was filtered hot and recrystallized from ethanol to give the pure compound of **5-n** and **6-n**.

### LC 5–4

Yield 78%; yellowish solid; UV  $\lambda_{\text{max}}$ : 268, 275, 349, 362 nm; IR  $\nu_{\text{max}}$ : 1254, 1609( $\nu_{\text{C}=\text{N}}$ ), 1725( $\nu_{\text{C}=\text{O}}$ ), 2872, 2956( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ .

**LC 5-6**

Yield 75%; yellowish solid; UV  $\lambda_{\text{max}}$ : 268, 275, 351 nm; IR  $\nu_{\text{max}}$ : 1252, 1605( $\nu_{\text{C}=\text{N}}$ ), 1731( $\nu_{\text{C}=\text{O}}$ ), 2869, 2941( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ .

**LC 5-7**

Yield 71%; yellowish solid; UV  $\lambda_{\text{max}}$ : 267, 275, 350 nm; IR  $\nu_{\text{max}}$ : 1254, 1608( $\nu_{\text{C}=\text{C}}$ ), 1725( $\nu_{\text{C}=\text{O}}$ ), 2854, 2919( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.54 (s, 2H), 8.13 (d,  $J = 8.7$  Hz, 4H), 8.03 (s, 4H), 7.30 (d,  $J = 8.7$  Hz, 4H), 7.27 (d,  $J = 8.7$  Hz, 4H), 6.96 (d,  $J = 8.8$  Hz, 4H), 4.05 (t,  $J = 6.5$  Hz, 4H), 1.85–0.88 (m, 26H, aliphatic **H**).

**LC 5-8**

Yield 72%; yellowish solid; UV  $\lambda_{\text{max}}$ : 268, 274, 349, 360 nm; IR  $\nu_{\text{max}}$ : 1254, 1607( $\nu_{\text{C}=\text{N}}$ ), 1727( $\nu_{\text{C}=\text{O}}$ ), 2853, 2921( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.54 (s, 2H), 8.14 (d,  $J = 8.7$  Hz, 4H), 8.02 (s, 4H), 7.30 (d,  $J = 8.7$  Hz, 4H), 7.24 (d,  $J = 8.7$  Hz, 4H), 6.97 (d,  $J = 8.8$  Hz, 4H), 4.03 (t,  $J = 6.5$  Hz, 4H), 1.85–0.88 (m, 30H, aliphatic **H**), MS  $m/z$  780 ( $\text{M}^+$ ); anal. Found (calculated)% for  $\text{C}_{50}\text{H}_{56}\text{O}_6\text{N}_2$ : C, 76.9 (76.8); H, 7.3 (7.2); N, 3.4 (3.6).

**LC 5-10**

Yield 78%; yellowish solid; UV  $\lambda_{\text{max}}$ : 268, 275, 350 nm; IR  $\nu_{\text{max}}$ : 1254, 1607( $\nu_{\text{C}=\text{N}}$ ), 1731( $\nu_{\text{C}=\text{O}}$ ), 2850, 2919( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ .

**LC 5-12**

Yield 82%; yellowish solid; UV  $\lambda_{\text{max}}$ : 268, 276, 354 nm; IR  $\nu_{\text{max}}$ : 1254, 1608( $\nu_{\text{C}=\text{N}}$ ), 1734( $\nu_{\text{C}=\text{O}}$ ), 2849, 2917( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.53 (s, 2H), 8.14 (d,  $J = 8.7$  Hz, 4H), 8.03 (s, 4H), 7.31 (d,  $J = 8.7$  Hz, 4H), 7.25 (d,  $J = 8.7$  Hz, 4H), 6.97 (d,  $J = 8.8$  Hz, 4H), 4.04 (t,  $J = 6.5$  Hz, 4H), 1.85–0.87 (m, 46H, aliphatic **H**).

**LC 5-14**

Yield 76%; yellowish solid; UV  $\lambda_{\text{max}}$ : 269, 275, 348 nm; IR  $\nu_{\text{max}}$ : 1255, 1608( $\nu_{\text{C}=\text{N}}$ ), 1733( $\nu_{\text{C}=\text{O}}$ ), 2849, 2917( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ .

**LC 6-6**

Yield 76%; yellowish solid; UV  $\lambda_{\text{max}}$ : 276, 326 nm; IR  $\nu_{\text{max}}$ : 1252, 1604( $\nu_{\text{C}=\text{N}}$ ), 1734( $\nu_{\text{C}=\text{O}}$ ), 2868, 2929( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.59 (s, 1H), 8.51 (s, 1H), 8.31 (d,  $J = 8.7$  Hz, 2H), 8.14 (d,  $J = 8.3$  Hz, 4H), 8.06 (d,  $J = 8.0$  Hz, 2H), 8.00 (d,  $J = 8.0$  Hz, 2H), 7.38 (d,  $J = 8.2$  Hz, 2H), 7.32 (d,  $J = 8.4$  Hz, 2H), 7.23–7.29 (m, 6H), 6.97 (d,  $J = 8.2$  Hz, 4H), 4.05 (t,  $J = 6.2$  Hz, 4H), 1.85–0.92 (m, 22H, aliphatic **H**).

**LC 6-7**

Yield 78%; yellowish solid UV  $\lambda_{\max}$ : 276, 324 nm; IR  $\nu_{\max}$ : 1254, 1604( $\nu_{\text{C}=\text{N}}$ ), 1734( $\nu_{\text{C}=\text{O}}$ ), 2855, 2926( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.61 (s, 1H), 8.52 (s, 1H), 8.32 (d,  $J = 8.7$  Hz, 2H), 8.14 (d,  $J = 8.3$  Hz, 4H), 8.07 (d,  $J = 8.0$  Hz, 2H), 8.01 (d,  $J = 8.0$  Hz, 2H), 7.45 (d,  $J = 8.2$  Hz, 2H), 7.38 (d,  $J = 8.4$  Hz, 2H), 7.23–7.30 (m, 6H), 6.98 (d,  $J = 8.2$  Hz, 4H), 4.04 (t,  $J = 6.2$  Hz, 4H), 1.85–0.90 (m, 26H, aliphatic **H**).

**LC 6-8**

Yield 72%; yellowish solid; UV  $\lambda_{\max}$ : 276, 327 nm; IR  $\nu_{\max}$ : 1254, 1605( $\nu_{\text{C}=\text{N}}$ ), 1733( $\nu_{\text{C}=\text{O}}$ ), 2853, 2924( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.59 (s, 1H), 8.51 (s, 1H), 8.32 (d,  $J = 8.7$  Hz, 2H), 8.14 (d,  $J = 8.3$  Hz, 4H), 8.05 (d,  $J = 8.0$  Hz, 2H), 8.00 (d,  $J = 8.0$  Hz, 2H), 7.38 (d,  $J = 8.2$  Hz, 2H), 7.33 (d,  $J = 8.4$  Hz, 2H), 7.28–7.30 (m, 6H), 6.97 (d,  $J = 8.2$  Hz, 4H), 4.04 (t,  $J = 6.2$  Hz, 4H), 1.85–0.88 (m, 30H, aliphatic **H**).

**LC 6-10**

Yield 75%; yellowish solid; UV  $\lambda_{\max}$ : 276, 326 nm; IR  $\nu_{\max}$ : 1254, 1604( $\nu_{\text{C}=\text{N}}$ ), 1732( $\nu_{\text{C}=\text{O}}$ ), 2852, 2921( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.59 (s, 1H), 8.51 (s, 1H), 8.32 (d,  $J = 8.7$  Hz, 2H), 8.14 (d,  $J = 8.3$  Hz, 4H), 8.06 (d,  $J = 8.0$  Hz, 2H), 8.00 (d,  $J = 8.0$  Hz, 2H), 7.38 (d,  $J = 8.2$  Hz, 2H), 7.33 (d,  $J = 8.4$  Hz, 2H), 7.28–7.29 (m, 6H), 6.97 (d,  $J = 8.2$  Hz, 4H), 4.04 (t,  $J = 6.2$  Hz, 4H), 1.84–0.87 (m, 38H, aliphatic **H**). MS  $m/z$  956 ( $\text{M}^+$ ), anal. found (calculated)% for  $\text{C}_{61}\text{H}_{68}\text{O}_8\text{N}_2$ : C, 76.5 (76.5); H, 7.2 (7.1); N, 3.0 (2.9).

**LC 6-12**

Yield 79%; yellowish solid; UV  $\lambda_{\max}$ : 277, 328 nm; IR  $\nu_{\max}$ : 1254, 1605( $\nu_{\text{C}=\text{N}}$ ), 1732( $\nu_{\text{C}=\text{O}}$ ), 2851, 2921( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.59 (s, 1H), 8.51 (s, 1H), 8.30 (d,  $J = 8.7$  Hz, 2H), 8.14 (d,  $J = 8.3$  Hz, 4H), 8.06 (d,  $J = 8.0$  Hz, 2H), 7.99 (d,  $J = 8.0$  Hz, 2H), 7.44 (d,  $J = 8.2$  Hz, 2H), 7.32 (d,  $J = 8.4$  Hz, 2H), 7.23–7.30 (m, 6H), 6.97 (d,  $J = 8.2$  Hz, 4H), 4.04 (t,  $J = 6.2$  Hz, 4H), 1.84–0.87 (m, 46H, aliphatic **H**).

**LC 6-14**

Yield 75%; yellowish solid; UV  $\lambda_{\max}$ : 277, 328 nm; IR  $\nu_{\max}$ : 1254, 1607( $\nu_{\text{C}=\text{N}}$ ), 1730( $\nu_{\text{C}=\text{O}}$ ), 2849, 2918( $\nu_{\text{CH}}$ )  $\text{cm}^{-1}$ .



## REFERENCES

- [1] Kelker, H. & Scheurle, B. (1969). *Angew. Chem. Int. Edn. Eng.*, 8, 884.
- [2] Gray, G. W., Harrison, K. J., & Nash, J. A. (1973). *Electron. Lett.*, 9, 130.
- [3] (a) Smith, G. W. & Gardlund, Z. G. (1973). *J. Chem. Phys.*, 59, 3214; (b) Rao, P. B., Rao, N. V. S., Pisipati, V. G. K. M. (1981). *Mol. Cryst. Liq. Cryst.*, 206, 9; (c) Goodby, J. W., Gray, G. W., Leadbetter, A. J., & Mazid, M. A. (1980). In: *Liquid Crystal of One and Two Dimensional Order*, Helfrich, W. & Heppke, G. (Eds.), Springer-Verlag: New York.
- [4] Richter, L., Demus, D., & Sackmann, H. (1981). *Mol. Cryst. Liq. Cryst.*, 71, 269.
- [5] Guillevic, M. A., Light, M. E., Coles, S. J., Gelbrich, T., Hursthouse, M. B., & Bruce, D. (2000). *J. Chem. Soc., Dalton Trans.*, 1437.
- [6] Guillevic, M. A., Danks, M. J., Harries, S. K., Collinson, S. R., Pidwell, A. D., & Bruce, D. (2000). *Polyhedron*, 19, 249.
- [7] Lakshminarayana, S., Prabhu, C. R., Potukuchi, D. M., Rao, N. V. S., & Pisipati, V. G. K. M. (1996). *Liq. Cryst.*, 20, 177.
- [8] Kajitani, T., Masu, H., Kohmoto, S., Yamamoto, M., Yamaguchi, K., & Kishikawa, K. (2005). *J. Am. Chem. Soc.*, 127, 1124.