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Liquid Crystals

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A. K. Prajapati[a]; Vishal Modi[a]
[a] Applied Chemistry Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara, India

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Bent-shaped mesogenic oxadiazole and thiadiazole derivatives from rod-shaped mesogenic hydrazide containing polar chloro group

A.K. Prajapati* and Vishal Modi

Applied Chemistry Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara 390 001, India

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Rod-shaped mesogenic hydrazide (series **I**) derivatives have been synthesised by the Schotten-Baumann reaction of 4-chlorobenzhydrazide with 4-*n*-alkoxybenzoyl chloride using pyridine as a solvent. Rod-shaped mesogenic hydrazide (series **I**) have been cyclised to bent-shaped mesogenic oxadiazole (series **II**) and thiadiazole (series **III**) derivatives using $POCl_3$ and P_2S_5, respectively. The synthesised compounds are characterised by a combination of elemental analysis and standard spectroscopic methods. All the compounds of present series **I–III** exhibit smectic A mesophase. The mesomorphic properties of the present series **I–III** are compared with each other and with the other structurally related mesogenic homologous series to evaluate the effect of bent-shape and different heterocyclic moiety on mesomorphism.

Keywords: oxadiazole; thiadiazole; bent-shaped; mesomorphism.

1. Introduction

Heterocyclic compounds like pyridine and pyrimidine derivatives [1] are valuable liquid crystalline materials for technical application. It has also been reported that a five-member thiadiazole or thiophene ring [2–5] may incorporate into the principal structure of calamitic mesogens. Interest in mesomorphic heterocyclic compounds [6] has dramatically increased due to their more diversified structural figures and distinct mesomorphic properties. Numerous unsaturated structures forming a variety of molecular shapes have been generated and found to exhibit interesting mesomorphic properties. Furthermore, significant compounds have a six-member or larger fused ring as a core group and the hetero-atoms incorporated including nitrogen, oxygen or sulphur are synthesised. Typical examples having such cores are the benzotrisfuran [7], ionic ditholium salts [8], and bispyran salts [9]. Usually, 5- or 6-membered heterocycles are involved, and they form part of the core in rod-shaped, bent-shaped or disc-shaped molecules. Many series of liquid crystalline compounds containing heterocyclic groups have been synthesised due to their potential wide range of application, such as in optical, electrical and biomedical fields [10,11]. Heterocyclic compounds such as five-member thiadiazole or thiophene rings can be incorporated into the principal structure of calamitic mesogens [12–17]. The 1, 3, 4-oxadiazole derivatives are well known for their high thermal and hydrolytic stability, resistance to oxidative degradation and electron-accepting properties [18]. 1, 3, 4-oxadiazole liquid crystal derivatives, having asymmetric structures within oxadiazole ring into the central position of the mesogenic rigid core, were first reported by Dimitrowa *et al.* [2]. However, comparison of these compounds with the analogous thiadiazole derivatives reveals that the replacement of the sulphur atom by oxygen causes a complete loss of liquid crystalline properties. Also, a series of asymmetric calamitic 1, 3, 4-oxadiazole-base liquid crystals containing different terminal polar units have been synthesised by Sung and Lin [19]. Compounds containing a 1, 3, 4-thiadiazole moiety have been extensively investigated because of their high quantum yield of luminescence, thermal stability and electron-transport properties [16]. Recently, synthesis, thermal properties and luminescence studies in solution and solid phase of twin dimers of 1, 3, 4-oxadiazoles containing an alkyl chain as a spacer have been reported by Srivastava *et al.* [20].

Rational design and synthesis of π-conjugated mesogenic molecules is an important research interest in the field of physics, chemistry, material science and engineering because these low molecular weight materials can be readily modified and exhibit interesting electronic, luminescent and liquid crystal properties, which favours the development of new functional materials in liquid crystal display, electronic and optoelectronic applications [21–23]. Liquid crystals, rod-like (calamitic) or bent-shaped, both shapes based on substituted 2, 5-diaryl-1, 3, 4-oxadiazole derivatives, have been extensively studied due to their

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*Corresponding author. Email: akprajapati@yahoo.co.uk

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good thermal and chemical stability, photoluminescence quantum yields and the electron deficient feature of the 1, 3, 4-oxadiazole ring [24–30]. Bent-core materials also generated a good deal of interest in the theoretical and computational communities, and a wealth of potential new phases have emerged from their treatments [30]. However, in most cases, 1, 3, 4-oxadiazole derivatives show narrow mesophase temperature range. In this regard, Watanabe *et al.* [31] reported different types of symmetric 1, 3, 4-oxadiazole derivatives containing biphenyl spacers and ester linkages, which produced mesophases with moderated mesomorphic temperature ranges of 191–261°C and 148–222°C, respectively. According to the general character of the liquid crystal structure, we know that phenyl-1, 3, 4-oxadiazole groups can be used as the rigid structural unit to form the base for the liquid crystal molecule. If an alkyl group of a certain length is added to such a structural unit, it is possible to design an electroluminescent molecule that possesses liquid crystalline properties.

In the present paper, we report the synthesis and characterisation of bent-shaped mesogenic oxadiazole and thiadiazole derivatives from rod-shaped mesogenic hydrazide containing the polar chloro group to evaluate the effect of the bent-shape and different heterocyclic moiety on mesomorphism.

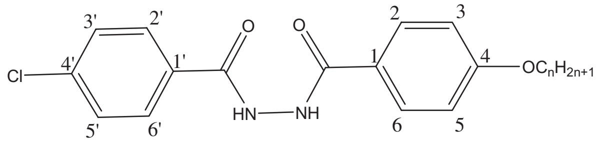
2. Experimental

The requisite starting materials such as 4-chlorobenzoic acid, methanol, sulphuric acid, hydrazine hydrate (99%), 1-bromoalkane, 4-hydroxybenzoic acid, phosphorus pentasulphide, phosphorus oxychloride, potassium hydroxide, ethanol, thionyl chloride, pyridine, hydrochloric acid, ethyl acetate, diethyl ether, hexane etc., were procured from Aldrich Company and used without any further purification. All the solvents were purified and dried by standard methods.

2.1 Characterisation

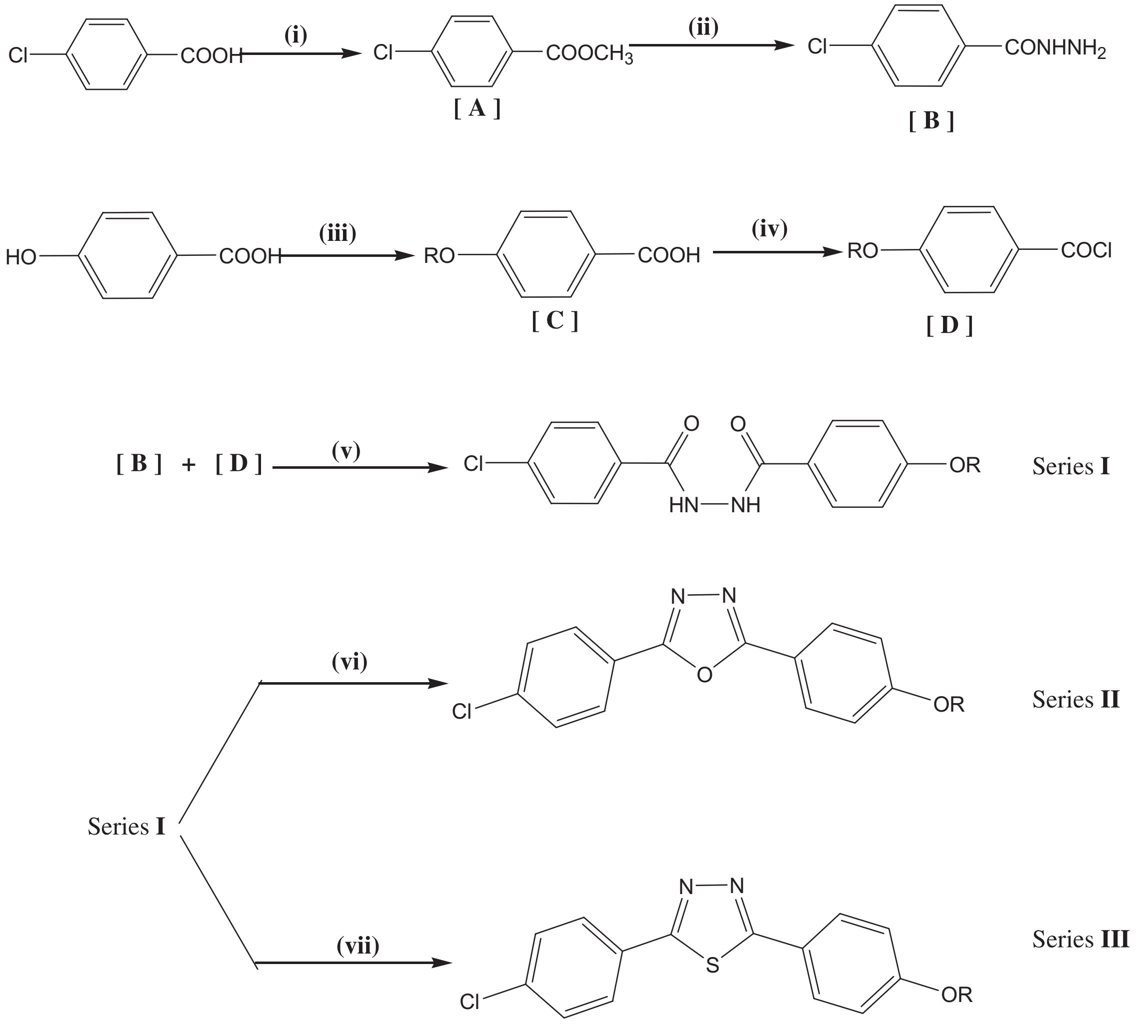
Microanalysis of the compounds was performed on a Coleman carbon–hydrogen analyser, and the values obtained are in close agreement with those calculated. IR spectra were determined for KBr pellets using a Shimadzu IR-408 spectrophotometer. ^{1}H NMR spectra were obtained with a Perkin-Elmer R-32 spectrometer using tetramethylsilane (TMS) as an internal reference standard. UV absorption spectra were obtained with Schimadzu-2450 spectrophotometer. The chemical shifts are quoted in parts per million downfield from the reference; DMSO-d_6 was used as the solvent for all the compounds. Liquid crystalline properties were investigated on a Leitz Laborlux 12 POL microscope equipped with a heating stage. The enthalpies of transitions, reported in J g^{-1}, were measured using differential scanning calorimetry (DSC) via a Mettler TA-4000 system at a scanning rate of 5°C min^{-1}. The calorimeter was calibrated using pure indium as standard. The synthetic routes to series **I-III** compounds are illustrated in scheme 1.

Methyl-4-chloro benzoate (**A**) and 4-chlorobenzhydrazide (**B**) were synthesised by the method reported by Olah *et al.* [32]. 4-*n*-Alkoxybenzoic acid (**C**) and 4-*n*-alkoxybenzoyl chloride **(D)** were synthesised by a modified method of Dave and Vora [33]. 4-Chlorobenzoic acid-N'-(4'-*n*-alkoxybenzoyl) hydrazide (series **I**) was synthesised by condensing equimolar quantity of 4-chlorobenzhydrazide (**B**) and 4-*n*-alkoxybenzoyl chloride (**D**) respectively, in dry pyridine. The reaction mixture was poured into cold aqueous (1:1) HCl. The solid material obtained was filtered off and was chromatographed on silica gel (100–200 mesh) using a mixture of ethyl acetate and hexane (20:80) as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallised repeatedly from alcohol until constant transition temperatures were obtained. The reaction products were obtained as off-white solids in 80–85% yield. The purity of all these compounds was checked by thin layer chromatography (Merck kieselgel 60F254 pre-coated plates). Elemental analysis, IR and ^{1}H NMR spectral data for the *n*-octyloxy and *n*-decyloxy derivatives as representative members of series **I** are given below.



Analysis data for $n = 8$; elemental analysis: calculated for $C_{22}H_{27}N_2O_3Cl$: C, 65.59; H, 6.70; N, 6.95%. Found: C, 65.38; H, 6.42; N, 6.85%. IR spectrum (KBr) ν_{max}/cm^{-1}: 3250 (br) (-NH- stretching), 2925, 2875, 1700 (-C=O-), 1650 (-NH-), 1610 (Aromatic), 1485, 1250, 1190, 1100, 850, 730 (C-Cl). ^{1}H NMR spectrum: **δ** 0.82 (t, 3H, $-CH_3$), 1.31–1.40 (m, 10H, 5 × $-CH_2-$) 1.71 (quant., 2H, Ar-O-C-CH_2-) 4.05 (t, 2H, -O-CH_2-), 6.99 (d, $J = 8.8$ Hz, 2H, Ar-H at C-3 and C-5), 7.58 (d, $J = 9.0$ Hz, 2H, Ar-H at C-3' and C-5'), 7.85–7.94 (m, 4H, Ar-H at C-2, C-6, C-2' and C-6'), 10.38 (s, 1H of amide), 10.61 (s, 1H of amide).

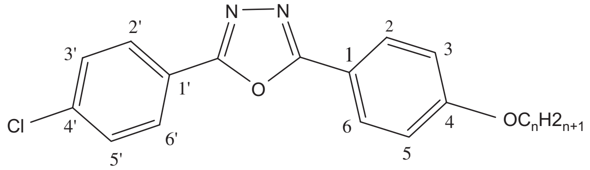
Analysis data for $n = 10$; elemental analysis: calculated for $C_{24}H_{31}N_2O_3Cl$: C, 66.89; H, 7.20; N, 6.50%. Found: C, 66.69; H, 7.01; N, 6.45 %. IR spectrum (KBr) ν_{max}/cm^{-1}: 3250 (br) (-NH- stretching), 2950, 2875, 1700 (-C=O-), 1680 (-NH-), 1600, 1470,



Scheme 1. Synthetic route to series I–III compounds.
Notes: R = -C_nH_{2n+1}, n = 5, 6, 7, 8, 10, 12, 14 and 16.
Reagent and conditions: (i) CH_3OH, H_2SO_4, reflux (ii) hydrazine hydrate, ethanol, reflux (iii) R-Br, alcoholic KOH, reflux (iv) $SOCl_2$ (v) pyridine, cold aqueous (1:1) HCl (vi) $POCl_3$, reflux (vii) P_2S_5, pyridine, reflux.

1270, 1175, 1100, 850, 740 (C-Cl). ^{1}H NMR spectrum: δ 0.82 (t, 3H, -CH_3), 1.24-1.40 (m, 14H, 7 × -CH_2-), 1.72 (quant., 2H, Ar-O-C-CH_2-) 4.02 (t, 2H, -O-CH_2-), 6.97 (d, J = 8.8 Hz, 2H, Ar-H at C-3 and C-5), 7.58 (d, J = 8.8 Hz, 2H, Ar-H at C-3' and C-5'), 7.84–7.94 (m, 4H, Ar-H at C-2, C-6, C-2' and C-6'), 10.37 (s, 1H of amide), 10.53 (s, 1H of amide).

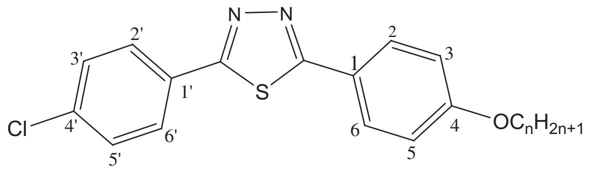
2-(4'-Chlorophenyl)-5-(4''-*n*-alkoxyphenyl)-1, 3, 4-oxadiazole (series **II**) was synthesised by refluxing 0.01 mole of series **I** compounds in an excess of phosphorus oxychloride. The reaction mixture was cooled to room temperature and then poured in to 100 g of ice. Obtained crude solid was filtered off and was chromatographed on silica gel (100–200 mesh) using a mixture of ethyl acetate and hexane (20:80) as eluent. Removal of the solvent from the eluate afforded a solid material, which was crystallised repeatedly from alcohol until constant transition temperatures were obtained. The reaction products were obtained as off-white solids in 75–80% yield. The purity of all these compounds was checked by thin layer chromatography (Merck kieselgel 60F254 pre-coated plates). Elemental analysis, IR and ^{1}H NMR spectral data for the *n*-octyloxy and *n*-decyloxy derivatives as representative members of series **II** are given below.



Analysis data for $n = 8$; elemental analysis: calculated for $C_{22}H_{25}N_2O_2Cl$: C, 68.66; H, 6.50; N, 7.28%. Found: C, 68.60; H, 6.39; N, 7.14%. IR spectrum (KBr) ν_{max}/cm^{-1}: 2950, 2875, 1610, 1595, 1500, 1450, 1405, 1300, 1250, 1175, 1100, 830, 725 (C-Cl). ^{1}H NMR spectrum: δ 0.90 (t, 3H, -CH_3), 1.25–1.55 (m, 10H, 5 × -CH_2-), 1.80(quant., 2H, Ar-O-C-CH_2-) 4.15 (t, 2H, -O-CH_2-), 7.25 (d, $J = 9.0$ Hz, 2H, Ar-H at C-3 and C-5), 7.80 (d, $J = 8.9$ Hz, 2H, Ar-H at C-3' and C-5'), 8.20 (d, $J = 9.2$ Hz, 2H, Ar-H at C-2 and C-6), 8.30 (d, $J = 9.0$ Hz, 2H, Ar-H at C-2' and C-6').

Analysis data for $n = 10$; elemental analysis: calculated for $C_{24}H_{29}N_2O_2Cl$: C, 69.81; H, 7.03; N, 6.78 %. Found: C, 69.65; H, 6.95; N, 6.61 %. IR spectrum (KBr) ν_{max}/cm^{-1}: 2950, 2875, 1610, 1595, 1500, 1450, 1405, 1300, 1250, 1175, 1100, 830, 725 (C-Cl). ^{1}H NMR spectrum: δ 0.90 (t, 3H, -CH_3), 1.25–1.55 (m, 14H, 7 × -CH_2-), 1.85 (quant., 2H, Ar-O-C-CH_2-) 4.15 (t, 2H, -O-CH_2-), 7.20 (d, $J = 8.7$ Hz, 2H, Ar-H at C-3 and C-5), 7.75 (d, $J = 9.0$Hz, 2H, Ar-H at C-3' and C-5'), 8.15 (d, $J = 9.0$ Hz, 2H, Ar-H at C-2 and C-6), 8.25 (d, $J = 8.8$ Hz, 2H, Ar-H at C-2' and C-6').

2-(4'-Chlorophenyl)-5-(4''-*n*-alkoxyphenyl)-1, 3, 4-thiadiazole (series **III**) was synthesised by refluxing equimolar quantities of series **I** compounds and phosphorus pentasulphide in excess of dry pyridine. The reaction mixture was cooled to room temperature and poured into 100 g of ice. The solid obtained was filtered off and chromatographed on silica gel (100–200 mesh) using mixture of ethyl acetate and hexane (30:70) as eluent. Removal of solvent from the eluate afforded a solid material, which was crystallised repeatedly from alcohol until constant transition temperatures were obtained. The reaction products were obtained as off-white solids in 75–80% yield. The purity of all these compounds was checked by thin layer chromatography (Merck kieselgel 60F254 pre-coated plates). Elemental analysis, IR and ^{1}H NMR spectral data for the *n*-octyloxy and *n*-decyloxy derivatives as a representative member of series **III** are given below.



Analysis data for $n = 8$; elemental analysis: calculated for $C_{22}H_{25}N_2OClS$: C, 65.91; H, 6.24; N, 6.99%. Found: C, 65.77; H, 6.17; N, 6.82%. IR spectrum (KBr) ν_{max}/cm^{-1}: 2950, 2875, 1610, 1525, 1500, 1475, 1450, 1400, 1300, 1260, 1180, 1100, 830, 725 (C-Cl). ^{1}H NMR spectrum: δ 0.84 (t, 3H,-CH_3), 1.24–1.60 (m, 10H, 5 x -CH_2-), 1.73 (quant., 2H, Ar-O-C-CH_2-) 4.10 (t, 2H, -O-CH_2-), 7.10 (d, $J = 9.0$ Hz, 2H, Ar-H at C-3 and C-5), 7.63 (d, $J = 9.0$ Hz, 2H, Ar-H at C-3' and C-5'), 7.93 (d, $J = 9.0$ Hz, 2H, Ar-H at C-2 and C-6), 8.03 (d, $J = 8.8$ Hz, 2H, Ar-H at C-2' and C-6').

Analysis data for $n = 10$; elemental analysis: calculated for $C_{24}H_{29}N_2OClS$: C, 67.21; H, 6.76; N, 6.53%. Found: C, 67.19; H, 6.55; N, 6.48%. IR spectrum (KBr) ν_{max}/cm^{-1}: 2950, 2875, 1600, 1540, 1500, 1475, 1450, 1400, 1300, 1260, 1180, 1100, 830, 720 (C-Cl). ^{1}H NMR spectrum: δ 0.84 (t, 3H, -CH_3), 1.24–1.55 (m, 14H, 7 × -CH_2-), 1.73 (quant., 2H, Ar-O-C-CH_2-), 4.07 (t, 2H, -O-CH_2-), 7.10 (d, $J = 8.9$ Hz, 2H, Ar-H at C-3 and C-5), 7.63 (d, $J = 9.0$ Hz, 2H, Ar-H at C-3' and C-5'), 7.93 (d, $J = 9.0$ Hz, 2H, Ar-H at C-2 and C-6), 8.03 (d, $J = 9.0$ Hz, 2H, Ar-H at C-2' and C-6').

3. Results and discussion

3.1 Optical microscopic studies

As a preliminary investigation, the mesophases exhibited by compounds of series **I–III** were examined by polarising optical microscopy (POM). Thin films of the samples were obtained by sandwiching them between a glass slide and cover slip. All the compounds of series **I–III** synthesised were found to exhibit mesomorphism. On cooling from the isotropic liquid, *n*-heptyloxy to *n*-hexadecyloxy derivatives of series **I** and **II** exhibited a focal conic texture of a smectic A mesophase (Plate 1(a) and 1(b)). In series

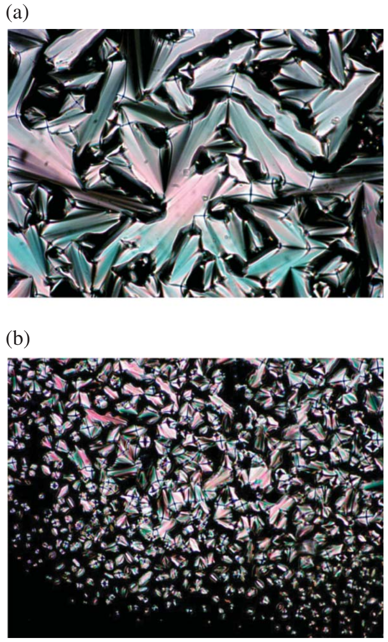


Plate 1. Optical micrographs of SmA mesophase (a) at 115°C and (b) at 125°C of *n*-decyloxy derivatives of series II on cooling (colour version online).

III, on cooling from the isotropic liquid, *n*-hexyloxy to *n*-hexadecyloxy derivatives exhibited a focal conic texture of a smectic A mesophase. There was no fundamental difference in the textures through derivatives of series **I–III**.

3.2 DSC studies

As representative cases, the phase transition enthalpies were measured for the *n*-octyloxy and *n*-decyloxy derivatives of series **I**, *n*-tetradecyloxy derivatives of series **II** and *n*-octyloxy derivatives of series **III** by DSC. The results are recorded in Table 1.

The mesophase assignments according to POM observation are in good agreement with the corresponding DSC thermograms. All compounds exhibit clear-cut transition temperatures in their DSC thermograms. On the heating scans, the DSC curve of series **I,** $n = 8$ showed two endothermic peaks at 147.18°C and 241.13°C, which were assigned to the crystal to smectic A and smectic A to isotropic liquid transitions, respectively. For $n = 10$, two endothermic peaks were seen at 140.21°C and 238.53°C, which were assigned to the crystal to smectic A and smectic A to isotropic liquid transitions, respectively. On the heating scans, the DSC curve of series **II,** $n = 14$ showed two endothermic peaks at 108.53°C and 125.59°C, which were assigned to the crystal to smectic A and smectic A to isotropic liquid transition, respectively. On the heating scans, the DSC curve of series **III,** $n = 10$ showed two endothermic peaks at 110.10°C and 235.61°C, which were assigned to the crystal to smectic A and smectic A to isotropic liquid transition, respectively.

3.3 UV studies

The UV absorption data for the solution of series **I–III** compounds in dichloromethane at 25°C are recorded in Table 2. For compounds of series **I**, a strong absorption band appeared at λ_{max} in the range of 240 nm to 245 nm and 275 nm to 280 nm. For compounds of series **II**, two absorption bands appeared at λ_{max} in the range of 245 nm to 250 nm and 300 nm to 305 nm. In compounds of series **III**, two absorption bands appeared at λ_{max} in the range of 225 nm to 230 nm and 300 nm to 315 nm.

Table 1. DSC data for series I–III compounds.

Series	*n*	Peak temperature (°C)	Transition state	ΔH (J g^{-1})	ΔS (J g^{-1} K^{-1})
I	8	147.18	Cr-SmA	16.03	0.0381
		241.13	SmA-I	4.33	0.0084
	10	140.21	Cr-SmA	15.84	0.0383
		238.53	SmA-I	5.40	0.0105
II	14	108.53	Cr-SmA	14.55	0.0381
		125.59	SmA- I	4.59	0.0115
III	10	110.10	Cr-SmA	12.58	0.0328
		235.61	SmA- I	5.30	0.0104

Table 2. UV data for series I–III.

	UV λ_{max}		
n	Series **I**	Series **II**	Series **III**
5	245, 278	250, 300	230, 310
6	250, 280	245, 305	230, 315
7	240, 275	248, 302	230, 310
8	242, 280	250, 300	225, 315
10	240, 275	245, 300	230, 315
12	242, 280	248, 300	230, 315
14	245, 280	250, 300	230, 305
16	240, 278	248, 300	230, 300

3.4 Phase behaviour

3.4.1 Series I: 4-Chlorobenzoic acid-N'-(4'-n-alkoxybenzoyl) hydrazide

Eight compounds of series **I** were synthesised and their mesogenic properties evaluated. Lower members ($n \leq 6$) do not exhibit mesomorphic property. However, higher members, *n*-heptyloxy to *n*-hexadecyloxy, exhibit an enantiotropic smectic A mesophase. The transition temperatures are recorded in Table 3. The plot of transition temperatures against number of carbon atoms in the alkoxy chain (Figure 1) exhibited little odd–even effect for *n*-heptyloxy and *n*-octyloxy derivatives, then showed decreasing tendency for smectic A–isotropic (SmA–I) transition temperatures up to the *n*-decyloxy derivative, which levels up until the last derivative synthesised.

3.4.2 Series II: 2-(4'-Chlorophenyl)-5-(4''-n-alkoxyphenyl) - 1, 3, 4-oxadiazole

Eight compounds of series **II** were synthesised and their mesogenic properties evaluated. Lower members ($n \leq 6$) are non-mesogenic. The *n*-Heptyloxy derivative exhibits a monotropic smectic A mesophase, while *n*-octyloxy to *n*-hexadecyloxy derivatives exhibit an enantiotropic smectic A mesophase. The transition temperatures are recorded in Table 3. The plot of transition temperatures against number of carbon atoms in the alkoxy chain (Figure 2) showed an initially rising tendency which may be due to usual odd–even effect, and then a falling tendency for smectic A–isotropic (SmA-I) transition temperatures.

Table 3. Transition temperature (°C) of the series I–III compounds.

Compound No.	*n*	Cr		SmA		I
Series **I**						
1	5	●	194			●
2	6	●	191			●
3	7	●	170	●	234	●
4	8	●	148	●	240	●
5	10	●	140	●	238	●
6	12	●	134	●	234	●
7	14	●	140	●	238	●
8	16	●	135	●	245	●
Series **II**						
9	5	●	155			●
10	6	●	124			●
11	7	●	132	(●	123)	●
12	8	●	103	●	128	●
13	10	●	104	●	126	●
14	12	●	103	●	123	●
15	14	●	105	●	122	●
16	16	●	103	●	118	●
Series **III**						
17	5	●	151			●
18	6	●	128	●	251	●
19	7	●	135	●	244	●
20	8	●	114	●	241	●
21	10	●	113	●	239	●
22	12	●	110	●	238	●
23	14	●	120	●	230	●
24	16	●	128	●	225	●

Note: Cr: Crystalline; SmA: Smectic A phase; I: Isotropic liquid; ●: Phase exist; (): Monotropic value.

3.4.3 Series III: 2-(4'-Chlorophenyl)-5-(4''-n-alkoxyphenyl)-1, 3, 4-thiadiazole

Eight compounds of series **III** were synthesised and their mesogenic properties evaluated. Lower members ($n \leq 5$) do not exhibit mesomorphic property. *n*-Hexyloxy to *n*-hexadecyloxy derivatives exhibit enantiotropic smectic A mesophase. The transition temperatures are recorded in Table 3. The plot of transition temperatures against number of carbon atoms in the alkoxy chain (Figure 3) exhibited a falling tendency for smectic A–isotropic (SmA–I) transition temperatures.

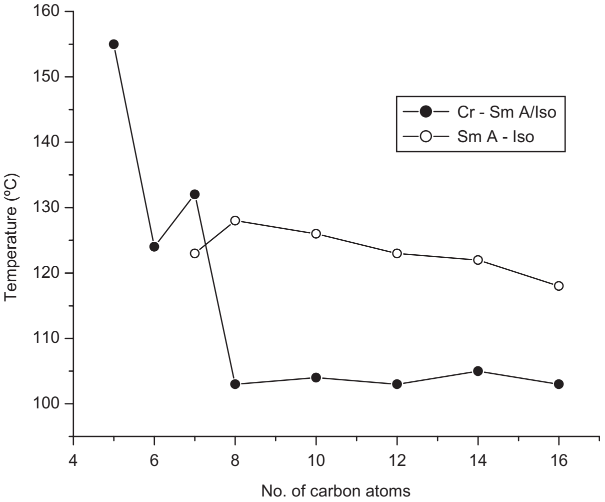


Figure 2. The phase behaviour of series II.

3.5 Mesogenic properties and molecular constitution

It is well known that thermotropic liquid crystals are highly sensitive to their molecular constitution. It is of prime importance, from the chemist's point of view, to determine the effects of alterations in the molecular core on the mesogenic properties of a compound. The thermal stability and mesophase length as a measure of mesomorphism can be correlated with the molecular constitution of the compounds. Figure 4

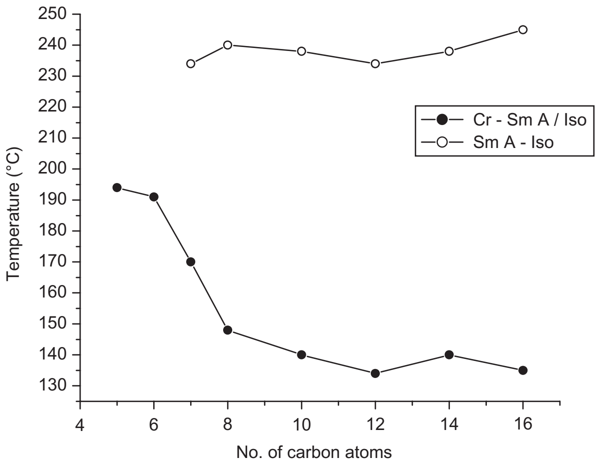


Figure 1. The phase behaviour of series I.

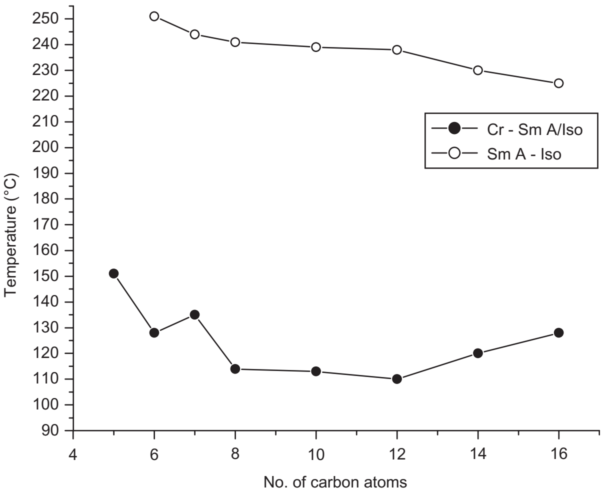


Figure 3. The phase behaviour of series III.

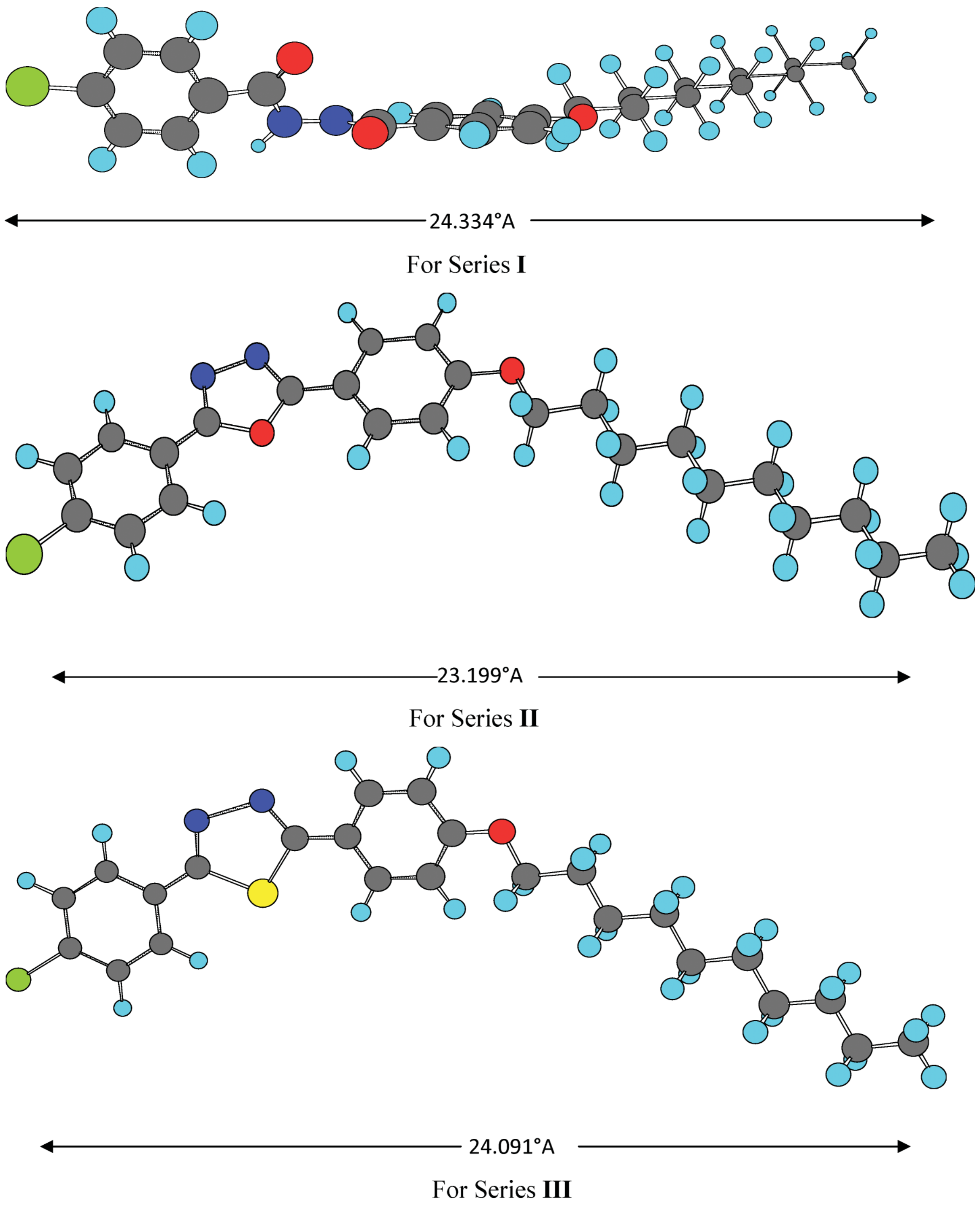
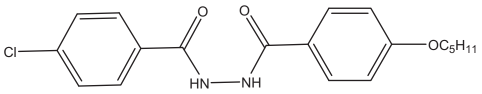
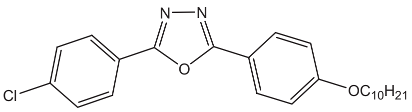


Figure 4. Energy-minimized Ball and stick model (MM2 models derived from CS Chem draw Ultra 7.0 software) structures of *n*-decyloxy derivative of series I–III (colour version online).

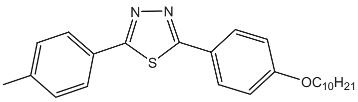
summarises the transition temperatures and molecular structure of the *n*-decyloxy derivative of the present series **I–III** (compounds **5**, **13** and **21**) and structurally related compounds **A**, **B**, **C** and **D** reported in the literature [34]. The smectic A mesophase length and thermal stabilities of the compound **5** is higher by 76°C and 112°C, respectively, than those of the compound **13**. From Figure 5, we can see that the molecular length of compound **5** (24.334 Å) is larger compared with compound **13** (23.199 Å). Compound **5** has rod-like linear geometry while compound **13** has bent-shape, which increases the breath of molecule. Gray



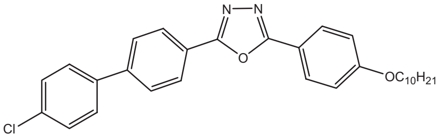
Compound **5:** Cr 140°C SmA 238°C Iso



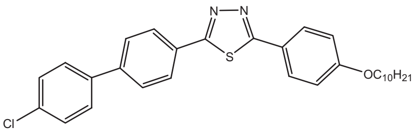
Compound **13:**Cr 104°C SmA 126°C Iso



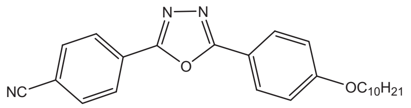
Compound **21:** Cr 113°C SmA 239°C Iso



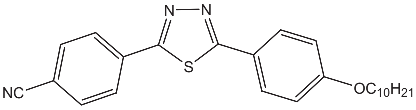
Compound **A**: Cr 111.4°C SmA 215.8°C Iso



Compound **B**: Cr 120.8°C SmA 369.1°C Iso



Compound **C**: Cr 128.1°C SmA 133.7°C Iso



Compound **D:** Cr 105.6°C SmA 260.4°C Iso

Figure 5. Transition temperatures and molecular structures of the present compounds 5, 13, 21 and structurally related compound A, B, C and D.

[35] has explained that an increase in the breadth of the molecules reduces smectic mesophase stability.

The smectic A mesophase length and thermal stabilities of compound **21** is higher by 28°C and 1°C, respectively, than those of the compound **5**. The long C-S bond distance and smaller C-S-C angle of the 1, 3, 4-thiadiazole unit favour the formation of a rod-like molecular geometry with large bent angle, which enables more efficient packing of the molecules and thus probably provides more thermal stability and greater mesophase length to compound **21** than that of compound **5**.

Reference to Figure 4 indicates that the smectic A mesophase length and thermal stabilities of the compound **21** is higher by 104°C and 113°C, respectively, than those of compound **13.** The lone pair of sulphur atoms of the thiadiazole ring involves no intermolecular interaction in the crystalline solids. Thus, for the same type of the terminal substituents, the melting temperatures of 1, 3, 4-thiadiazole derivatives and the corresponding 1, 3, 4-oxadiazole analogue are very near to each other, which might be related to the structural resemblance in their crystalline solids. The sulphur or oxygen atom of the thiadiazole or oxadiazole ring plays a role in alternating the molecular shape, leading to different thermal stabilities of liquid crystalline behaviours. The long C-S bond distance and smaller C-S-C angle of the 1, 3, 4-thiadiazole unit favour the formation of a rod-like molecular geometry (Figure 5) with large bent angle, which enables more efficient packing of the molecules in the respective mesophase, compared with the bent-shaped 1, 3, 4-oxadiazole. The linearity of the molecule generates a larger dipole moment and therefore 1, 3, 4-thiadiazole analogues have greater mesophase temperature ranges as well as higher thermal stabilities compared with 1, 3, 4-oxadiazole.

Figure 4 also indicates that the smectic A mesophase length and thermal stabilities of compound **A** are higher by 82.4°C and 89.8°C, respectively, than those of the compound **13.** The difference in the molecular geometry between compounds **13** and **A** lies in the number of phenyl rings. The presence of an additional phenyl ring in compound **A** due to the biphenyl moiety increases the molecular length and overall polarisability of the molecule, which is responsible for the greater smectic A mesophase length and higher thermal stabilities of compound **A.** This is also reflected in the comparison of compounds **21** and **B**. The smectic A mesophase length and thermal stabilities of the compound **B** are higher by 127.5°C and 130.1°C, respectively, than those of compound **21.**

Figure 4 shows that the smectic A mesophase length of compound **C** is lower by 16.4°C and the smectic A mesophase thermal stability is higher by 7.7°C, respectively, than those of compound **13**. Reference to the molecular structure shows that compound **C** differs only at one terminus from compound **13**. Compound **C** has a cyano terminal substituent instead of the chloro of compound **13**. The higher smectic A–isotropic transition temperatures of compound **C** may be due to the more polar nature of the terminal cyano group, which increases the overall polarisability of the molecules of compound **C** compared with compound **13**. The range and thermal stability of the mesophase is a more important factor in relating mesomorphic behaviour to chemical constitution, since the chemical grouping gives rise to intermolecular attractions which in turn determine the mesophase range and thermal stability. One should remember too that the length of the mesophase is determined partly by the Cr–SmA transition temperatures. This is also reflected in the comparison of compounds **21** and **D.** The smectic A mesophase length and thermal stabilities of the compound **D** are higher by 28.8°C and 21.4°C, respectively, than those of compound **21.**

4. Conclusion

In this article we have presented the synthesis and characterisation of a mesogenic homologous series of rod-shaped hydrazide (series **I**) as well as bent-shaped oxadiazole (series **II**) and thiadiazole (series **III**) derivatives containing a polar chloro group. All the mesogenic homologous series **I–III** exhibit enantiotropic smectic A phase. The mesomorphic properties exhibited by the present series **I** and **II** show that the members of series **I** exhibit higher mesophase thermal stability as compared with those of series **II** due to their linear geometry. All the derivatives of the present mesogenic homologous series of thiadiazole exhibit higher mesophase thermal stabilities as compared with the oxadiazole analogue. All the derivatives of both the present mesogenic homologous series **II** and **III** exhibit lower mesophase thermal stabilities as compared with the biphenyl analogue due to the lower number of phenyl rings in the series **II** and **III** as compared with the biphenyl analogue.

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