λ-Shaped azomesogens with polar chloro- and nitro-substituents

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A new homologous series of λ-shaped mesogenic azo esters with polar chloro- and nitro- substituents has been synthesised by attaching a rigid 2-chloro-4-nitrophenylazo group to a resorcinol moiety by a central azo linkage. Both phenolic hydroxyl groups are esterified by 4-n-alkoxybenzoyl groups. All the compounds synthesised have been characterised using a combination of elemental analysis and standard spectroscopic methods. The mesomorphic properties of the compounds have been determined by polarising optical microscopy and differential scanning calorimetry. The lower members of the series are non-mesogenic, the middle members exhibit a nematic mesophase, and higher members exhibit a smectic A mesophase. The effect of polar chloro-, nitro-, and long lateral aromatic substituents, on mesomorphism is discussed.

Keywords: λ-shaped; azomesogens; smectic A; nematic

1. Introduction

A wide variety of liquid crystal (LC) compounds have been reported in the past, particularly since the 1960s, but recently it has been non-conventional LC [1–8] compounds which have attracted the most interest. Published research shows that a number of approaches have been adopted to design molecules of a variety of shapes which exhibit LC behaviour. In addition to a linear combination of two mesogens, other modes of interlinking can be visualised, including side-on linked H-shaped [5–7] and T-shaped [8–10] molecules. More recently, with the discovery of banana-shaped liquid crystals, in which bent molecules provide the core, the incorporation of non-linear units has gained additional importance.

U-shaped liquid crystals have been investigated by a number of research groups [11–13]. Attard and Douglass [13] have reported structure–property correlations in dimeric compounds derived from phthalic acid, providing important insights into U-shaped LC systems. Yoshizawa and Yamaguchi [14] have reported layered structure in the nematic phase consisting of U-shaped molecules. Recently Yoshizawa *et al.* [15] have reported the synthesis and physical properties of novel S-shaped LC oligomers in which two U-shaped mesogenic molecules are connected. Yoshizawa *et al.* [16] have also reported novel Y-shaped LC oligomers in which three mesogenic units are connected by 3,5-dihydroxybenzoic acid. Y-shaped LC oligomers are found to exhibit only an anticlinic SmC anti (SmC) phase. They have observed that the transition behaviour of the Y-shaped compounds is quite different from that of the corresponding λ-shaped mesogenic compounds.

Yamaguchi *et al.* [17] have separately reported the synthesis of a homologous series of novel λ-shaped mesogenic compounds in which three mesogenic groups are connected by means of 3,4-dihydroxybenzoic acid. They have investigated the physical properties of these λ-shaped mesogenic compounds using differential scanning calorimetry (DSC), X-ray diffraction measurements and optical microscopy. Earlier Vora *et al.* [18] have reported the synthesis and mesogenic properties of two λ-shaped mesogenic homologous series, in which one series has a methyl and the other an ethoxy terminal substituent. Mahajan *et al.* [19] report the synthesis of two λ-shaped mesogenic homologous series of 1,2,4-trisubstituted benzene derivatives possessing ester and amide linkages and terminal chloro or methoxy groups. Similarly, Ganatra and Bhoya [20] have reported the synthesis of a λ-shaped mesogenic homologous series possessing ester and azo linkages and terminal acetyl substituents. The λ-shaped molecular topology can be expected to produce its own characteristic effects since two separate non-symmetric molecular configurations co-exist in a single molecule.

In the present study, a novel λ-shaped mesogenic homologous series of azo esters containing polar chloro and nitro substituents has been synthesised, and the effect of these substituents on mesomorphism has been evaluated, in addition to the influence of a long lateral aromatic moiety.

2. Experimental

Starting materials, including 4-hydroxybenzoic acid and the relevant 1-bromoalkanes (BDH), potassium

hydroxide, resorcinol, 2-chloro-4-nitroaniline and thionyl chloride (Sisco), were used as received. All solvents were distilled and dried prior to use.

2.1   Characterisation

Microanalysis of the new compounds was carried out using a Coleman carbon–hydrogen analyser and the values obtained confirmed to be in close agreement with those calculated. Infrared (IR) spectra were determined on KBr pellets using a Shimadzu FTIR–8400 spectrophotometer. [1]H nuclear magnetic resonance (NMR) spectra were obtained on a Perkin–Elmer R–32 spectrometer using tetramethylsilane as internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference. Hexadeuterodimethyl sulfoxide was used as the solvent for all the compounds. Absorption spectra were recorded on a Shimadzu UV–Vis 2450 spectrometer. Liquid crystalline properties were investigated on a Leitz Laborlux

12 POL microscope provided with a heating stage. The enthalpies of transitions, reported as kJ/mol, were measured on a Mettler TA–4000 system with heating and cooling, at a scanning rate of $5°C \ min^{-1}$. The instrument was calibrated using pure indium as standard.

2.2   Synthesis

Compounds in the novel series **I–n** were prepared following the pathway indicated in Scheme 1.

2.2.1   2-Chloro-4-nitro-2′, 4′-dihydroxyazobenzene (B)

Compound **B** was synthesised using conventional diazotisation of 2-chloro-4-nitroaniline (**A**) and coupling with resorcinol [21]. The crude compound was repeatedly crystallised from ethanol to constant melting point (197°C).

Found C: 40.11, H: 2.67, N: 14.44%; $C_{12}H_8N_3O_4Cl$ requires C: 40.06, H: 2.73, and N: 14.31%. The IR
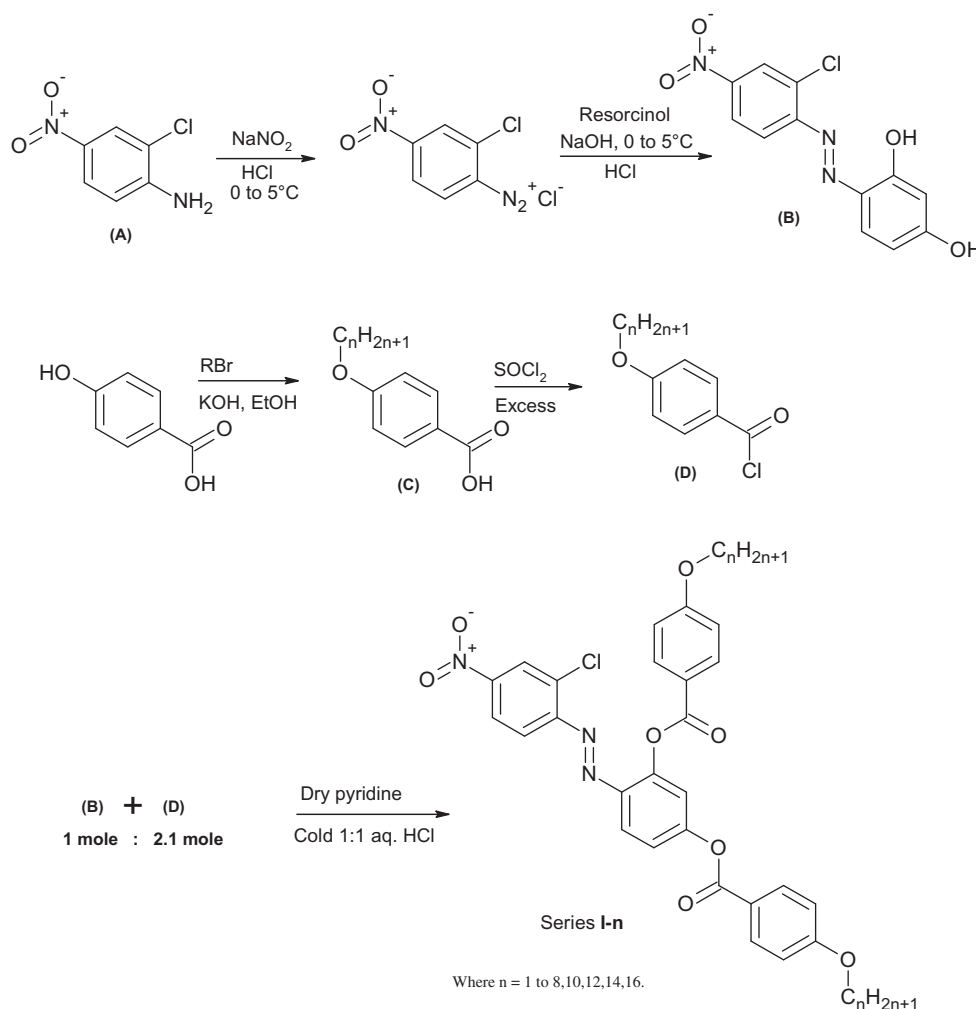
Scheme 1. Synthetic route to compounds in the series **I–n.**

spectrum of the compound showed a broad peak indicating intermolecular hydrogen-bonded phenolic OH between 3500 and 3300 cm^{-1}. Other signals were observed at 2921, 1610 (–N=N–), 1589, 1502 (–NO$_2$), 1475, 1406, 1305 (–NO$_2$), 1273, 1247, 1192, 1120, 1035, 877, 839, 658, 565 (C–Cl) cm^{-1}.

2.2.2 *4-n-Alkoxybenzoic acids (C) and 4′;-n-alkoxybenzoyl chlorides (D)*

These compounds were synthesised using a modification of the method of Dave and Vora [22].

2.2.3 *2-Chloro-4-nitro-2′,4′-bis(4-n-alkoxybenzoyloxy) azobenzenes (Series I–n)*

Compound **B** (0.02 mol) was dissolved in dry pyridine (5 ml) and a solution of compound **D** (0.042 mol) in cold dry pyridine (5 ml) was added slowly in an ice bath under constant stirring. The mixture was allowed to stand overnight at room temperature and was then acidified using cold 1 : 1 aqueous hydrochloric acid. The solid which separated was dried and triturated by stirring 30 min in 10% aqueous sodium hydroxide, and then washed with water. The insoluble product, free from reactants, was chromatographed on silica gel in a petroleum ether (60–80°C)-ethyl acetate mixture (98 : 2) as eluent. Removal of solvent from the eluate yielded a solid material which was repeatedly crystallised from ethanol until constant transition temperatures were obtained.

The purity of all these compounds was checked by thin-layer chromatography using aluminium sheets pre-coated with silica gel (Merck, Kieselge 60, F$_{254}$). The composition of all compounds was confirmed by elemental analysis (Table 1). UV–Vis, IR and ^{1}H NMR spectra for the *n*-hexyloxy derivative (**I–6**) and *n*-dodecyloxy derivative (**I–12),** as representative members of the series **I–n,** are shown in Table **2**.

3. Results and discussion

Twelve compounds were synthesised and their mesogenic properties evaluated using optical microscopy and DSC. Their transition temperatures and enthalpies are listed in Table 3. The first three members (*n* = 1, 2 and 3) of the series **I–n** are non-mesogenic. On cooling the isotropic liquids on an ordinary slide, the *n*-butyloxy to *n*-heptyloxy derivatives of the series **I–n** gave small droplets that coalesced into the threaded texture characteristic of the nematic mesophase (Figure 1(a)). On heating and cooling, only the *n*-octyloxy and *n*-decyloxy derivatives exhibited the focal conic texture characteristic of the SmA mesophase (Figure 1(b)), but the *n*-dodecyloxy to *n*-hexadecyloxy derivatives formed this focal conic texture when cooled from the isotropic liquid. The SmA phase of compound **I–12** showed a focal conic fan and isotropic texture under homogeneous (Figure 1(c)) and homeotropic (Figure 1(d)) alignment, respectively, under shear. There was no fundamental difference in texture throughout the series of derivatives.

A plot of transition temperatures against the number of carbon atoms in the alkoxy chain showed a smooth fall (Figure 2), with a pronounced odd–even effect for the I–N transition temperatures with increasing chain length. The I–SmA transition temperature also fell as the series ascended (Table 3). The sharp fall in I–SmA transition temperature between **I–10** and **I–12** is interesting. The slight change in the alkyl chain might have caused a significant change in the organisation of the λ-shaped molecules in the SmA phase, and this could be reflected in the sharp fall in the I–SmA transition. The sharp fall in I–SmA transition between **I–10** and **I–12** resulted in monotropic behaviour for the final three homologues.

Figure **3** shows the molecular shape of compounds **I–8** in the all-*trans* conformation, from which it will be observed that the molecules are neither rod-like nor

Table 1. The elemental analysis of the series **I–n** compounds (**n**: methylene number).

Compound **I–n**	Chemical formula	Required % (found %)		
		C	H	N
I–1	C$_{28}$H$_{20}$N$_3$O$_8$Cl	62.00 (62.13)	3.69 (3.48)	7.76 (7.80)
I–2	C$_{30}$H$_{24}$N$_3$O$_8$Cl	63.26 (63.09)	4.22 (4.15)	7.38 (7.54)
I–3	C$_{32}$H$_{28}$N$_3$O$_8$Cl	64.32 (64.27)	4.69 (4.59)	7.03 (7.15)
I–4	C$_{34}$H$_{32}$N$_3$O$_8$Cl	65.28 (65.17)	5.12 (5.09)	6.72 (6.80)
I–5	C$_{36}$H$_{36}$N$_3$O$_8$Cl	66.16 (65.99)	5.51 (5.55)	6.43 (6.45)
I–6	C$_{38}$H$_{40}$N$_3$O$_8$Cl	66.96 (66.89)	5.87 (5.70)	6.16 (6.11)
I–7	C$_{40}$H$_{44}$N$_3$O$_8$Cl	67.70 (67.65)	6.20 (6.15)	5.92 (5.87)
I–8	C$_{42}$H$_{48}$N$_3$O$_8$Cl	68.38 (68.29)	6.51 (6.25)	5.96 (5.88)
I–10	C$_{46}$H$_{56}$N$_3$O$_8$Cl	69.60 (69.40)	7.06 (6.96)	5.29 (5.19)
I–12	C$_{50}$H$_{64}$N$_3$O$_8$Cl	70.67 (70.57)	7.53 (7.29)	4.94 (4.76)
I–14	C$_{54}$H$_{72}$N$_3$O$_8$Cl	71.60 (71.56)	7.95 (7.68)	4.64 (4.57)
I–16	C$_{58}$H$_{80}$N$_3$O$_8$Cl	72.42 (72.39)	8.32 (8.22)	4.37 (4.29)

Table 2. The spectral data of the *n*–hexyloxy (**I–6**) and *n*–dodecyloxy (**I–12**) derivatives.

| Compound (**I–n**)	UV–Visible (nm)	FT–IR (ν_{max} cm^{-1})	^{1}H NMR (400 MHz)
I–6	260, 368 and 475	2920, 1737 (–COO–), 1602 (–N=N–), 1537, 1510 (–NO$_2$), 1577, 1420, 1305 (–NO$_2$), 1247, 1137, 1053, 839, 723, 685, 621, 532 (–C–Cl)	δ 0.83 (t, J = 6.7Hz, 6H, 2 × –CH$_3$), 1.2–1.4 (m, 12H, 6 × –CH$_2$–), 1.74 (qunt., 4H, 2 × –O–C–CH$_2$–), 4.0 (t, J = 6.8Hz, 4H, 2 × Ar–OCH$_2$–), 7.11–7.13 (m, 5H, ArH), 7.38 (d, J = 8.8Hz, 1H, ArH), 7.64 (d, J = 8.9Hz, 1H, ArH), 7.76–7.78 (m, 4H, ArH), 8.08–8.29 (m, 2H, ArH), 8.30 (s, 1H, ArH).
I–12	260, 365 and 470	2918, 1735 (–COO–), 1602 (–N=N–), 1529, 1510 (–NO$_2$), 1540, 1417, 1300 (–NO$_2$), 1238, 1120, 1059, 848, 759, 690, 632, 538 (–C–Cl).	δ 0.84 (t, J = 6.9Hz, 6H, 2 × –CH$_3$), 1.2–1.4 (m, 44H, 22 × –CH$_2$–), 1.7 (qunt., 4H, 2 × –O–C–CH$_2$–), 4.0 (t, J = 6.2Hz, 4H, 2 × Ar–OCH$_2$–), 7.03 (d, J = 9.0Hz, 4H, ArH), 7.10 (s, 1H, ArH), 7.12 (d, J = 9.1Hz, 1H, ArH), 7.64 (d, J = 8.9Hz, 1H, ArH), 7.90–8.00 (m, 4H, ArH), 8.03–8.32 (m, 2H, ArH), 8.31 (s, 1H, ArH).
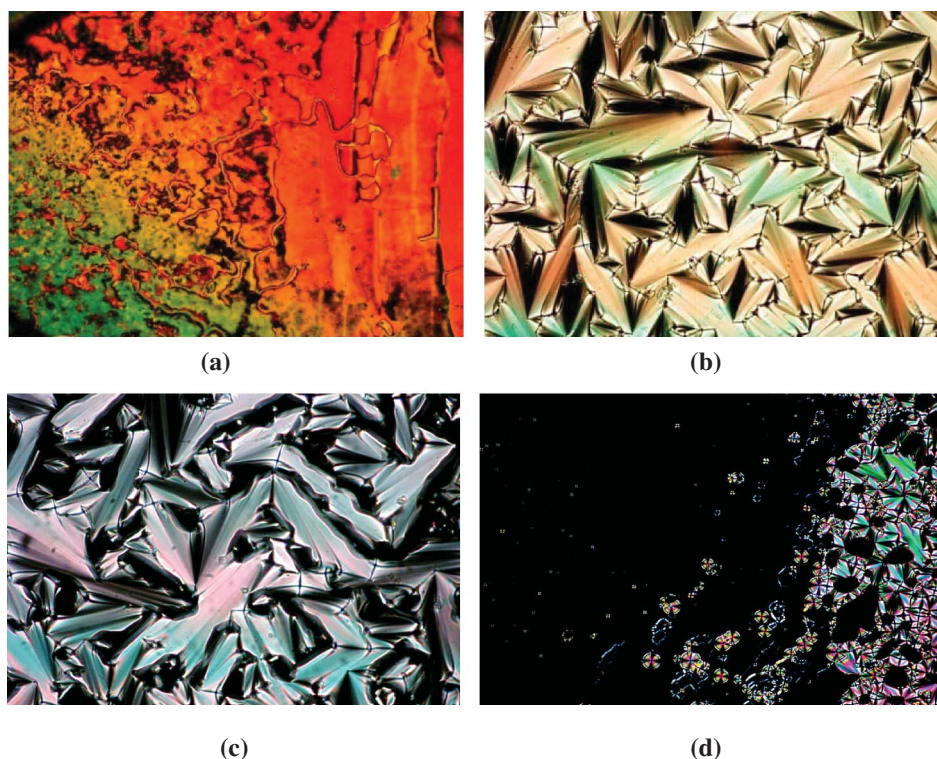
Figure 1. Optical micrographs of **(a)** N phase at 90°C of **I–7, (b)** SmA phase at 115°C of **I–10, (c)** SmA phase at 55°C of **I–12,** and **(d)** homeotropic alignments of **I–12** at 55°C (colour version online).

disc-like. Simply considering the length to breadth ratio of these λ-shaped molecules does not provide a complete explanation of the occurrence of an anisotropic liquid.

It is well known that thermotropic liquid crystals are highly sensitive to molecular composition. It is of paramount importance to the chemist to be able to understand the effect of the alteration in molecular core on the mesogenic properties of the compound. The thermal stability (transition temperature) and mesophase length as a measure of mesomorphism can

be correlated with the molecular constitution of the compound. Figure 4 summarises the transition temperatures, molecular structure and dimensions of compounds **I–8,** and other structurally related compounds, **II** [23], **III** [24] and **IV** [25], chosen for comparison.

The molecular geometry of compounds **I–8** comprises three phenyl rings linked by –COO– and –N=N– linkages, with a *n*-alkoxy group at one terminal and also at the lateral aromatic branch on the central benzene nucleus. The compound **II** has a lateral methyl
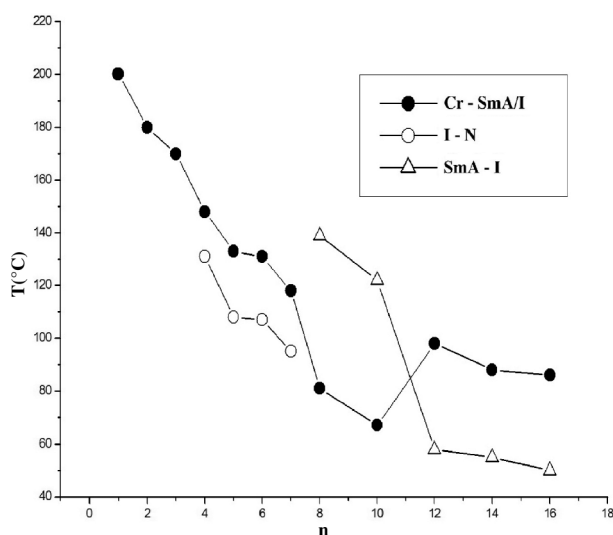
Figure 2. The phase behaviour of series **I–n** compounds.

Table 3. Transition temperatures (°C) and enthalpies [kJ/mol] of the compounds **I–n.**

Compound (I–n).	Heating	Cooling
I–1	Cr 200 Iso	Iso198 Cr
I–2	Cr 180 Iso	Iso 179 Cr
I–3	Cr 170 Iso	Iso168 Cr
I–4	Cr 143 [37.1] Iso	Iso 131 [1.4] N 49 [28.6] Cr
I–5	Cr 133 [29.6] Iso	Iso 108 [2.6] N 60 [23.8] Cr
I–6	Cr 131 [41.7] Iso	Iso 107 [2.7] N 65 [39.7] Cr
I–7	Cr 118 [53.4] Iso	Iso 95 [1.8] N 51 [38.3] Cr
I–8	Cr 81 [44.6] SmA 139 [6.7] Iso	Iso 139 [5.9] SmA 76 [43.8] Cr
I–10	Cr 67 [39.1] SmA 122 [4.1] Iso	Iso 120 [3.9] SmA 63 [40.2] Cr
I–12	Cr 98 [47.9] Iso	Iso 58 [3.6] SmA 21 [43.6] Cr
I–14	Cr 88 [56.5] Iso	Iso 55 [5.1] SmA 23 [51.9] Cr
I–16	Cr 86 [40.8] Iso	Iso 50 [4.7] SmA 22 [31.3] Cr

Notes: Cr: crystalline solid phase; SmA: smectic A phase; N: nematic phase; Iso: isotropic liquid phase.

group in place of the lateral aromatic branch in compound **I–8**. Comparing the mesomorphic characteristics of compound **I–8** and compound **II**, it is observed that **I–8** exhibits only the enantiotropic SmA mesophase, whereas compound **II** exhibits only the nematic mesophase enantiotropically. Moreover, the mesophase range of compound **I–8** is wider by 12°C, and its thermal stability (SmA–N/I transition temperature) is 6°C lower than that of compound **II**. The molecules of compound **I–8** and compound **II** differ only in the attachment of the lateral group. It seems that the lateral aromatic branch in compound **I–8** adversely affects the mesophase thermal stability to a greater extent than the lateral methyl group in compound **II,** presumably due to the effect of its increased breadth. It can be seen from Figure 4 that the L/D ratio in compound **I–8** (1.325) is lower than in compound **II** (1.998) due to the presence of the lateral *n*-alkoxybenzoyl substituent, which may be responsible for the slightly lower mesophase–isotropic transition temperature of compound **I–8**. The range and thermal stability of the mesophase is the 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 also remember that the length of the mesophase is determined partly by the Cr–N transition temperature.

Figure 4 also indicates that the SmA mesophase range of compound **I–8** is wider by 17°C than that of compound **III**, and the SmA–I transition temperature is also higher by 27°C than that of compound **III**. Compounds **I–8** and **III** differ only in the lateral group at one end. Compound **I–8** has a lateral –Cl group *meta* to the –NO$_2$ group, whereas the position *meta* to the –NO$_2$ group in compound **III** is unsubstituted. The lateral substitution in the molecule normally decreases the thermal stability of both the smectic and nematic mesophases, as a result of the broadening effect forcing the molecules apart. It seems that in compound **I–8** the lateral chloro substituent does not decrease the thermal stability of the SmA mesophase, but actually increases it due to the dipolar and polarisability effect of the substituent, without the counteracting breadth-increasing effect. Owing to the λ-shaped structure there is not much difference in L/D ratio between compound **I–8** (1.325) and compound **III** (1.350). The chloro substituent in compound **I–8** may simply occupy the gap between neighbouring molecules.

Lateral substituents which do not broaden the molecule enhance liquid crystal thermal stability; the thermal stability of the smectic phase is particularly enhanced when the substituent is dipolar. Gray [26] has explained that a compound which requires more thermal energy to disorganise the molecular arrangement of the smectic mesophase will be more thermally stable. As can be seen from Figure 4, more thermal energy has to be supplied to disorganise the molecular arrangement of the smectic melt of compound **I–8**, and as a result the SmA–I transition temperature is 27°C higher than that of compound **III**. Thus, the higher smectic–isotropic transition temperatures and mesophase width of compound **I–8** may be due to the polar nature of the lateral chloro group, which increases the overall polarisability
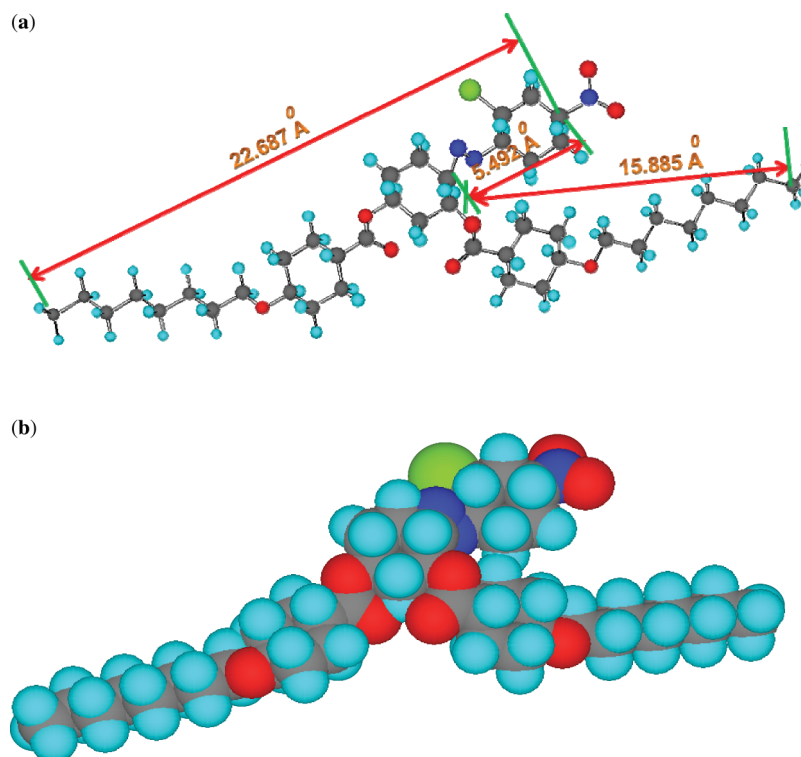
Figure 3. Energy-minimised (**a**) ball and stick model and (**b**) space-filling model structures of *n*-octyloxy derivative (**I–8**). (MM2 models derived using CS Chem-draw Ultra 7.0 software) (colour version online).

of the molecules of compound **I–8** compared to that of compound **III**.

Figure 4 indicates that compound **I–8** is purely smectogenic, whereas compound **IV** is purely nematogenic. Again, the molecules of compound **I–8** and **IV** differ only in the presence of substituents at one end. Compound **I–8** has a terminal –NO$_2$ and a lateral –Cl group *ortho* and *para* to the central azo linkage, respectively, whereas in compound **IV** the terminal phenyl ring is unsubstituted. It seems that polar –NO$_2$ and –Cl substituents must enhance the lateral attraction sufficiently for smectic mesophase formation to occur. Moreover, the SmA–I transition temperature of compound **I–8** is increased by 51°C compared with the N–I transition temperature of compound **IV**. This is understandable, since the *L*/*D* ratio of compound **I–8** (1.325) is higher than that of compound **IV** (1.209), and the molecules of compound **I–8** are also more polarisable than those of compound **IV** due to the presence of highly polar nitro and chloro substituents. The entire mesogenic homologous series of compound **IV** is purely nematogenic, whereas the presence of polar nitro- and chloro-substituents in the molecule of the mesogenic homologous series induces smectogenic characterisitcs.

The presence of azo groups leads to the possibly of photo-isomerisation and photochromic behaviour.

Preliminary studies of the photochemical properties were therefore conducted in solution. Chloroform solutions of concentration, $c = 2.4 \times 10^{-3}$ g dm^{-3}, for compound **I–6,** and $c = 2.3 \times 10^{-3}$ g dm^{-3} for compound **I–12,** were prepared for determination of UV–Vis absorption spectra. The λ-shaped mesogenic compounds displayed three primary absorption maxima, at 260 nm, 365–368 nm and 470–475 nm (Figure 5). The λ-shaped azo compounds in the *trans*-form show a strong band at ~365 nm attributed to π–π* transition, and a weak band at ~470 nm due to n–π* transition. The *trans*-form is much more stable than the *cis*-form, but each isomer can be transformed into the other by irradiation of light of the appropriate wavelength.

In general, on irradiation with UV light azobenzene compounds are characterised by a reversible transformation from the more stable *trans*- to the less stable *cis*-form. Linearly polarised light can induce the reorientation of azobenzene groups through photochemical *trans–cis–trans* isomerisaton [27–30].

4.   Conclusions

Twelve mesogenic λ-shaped homologues with polar nitro- and chloro-substituents have been synthesised. All the compounds have been characterised by elemental analysis and standard spectroscopic methods.
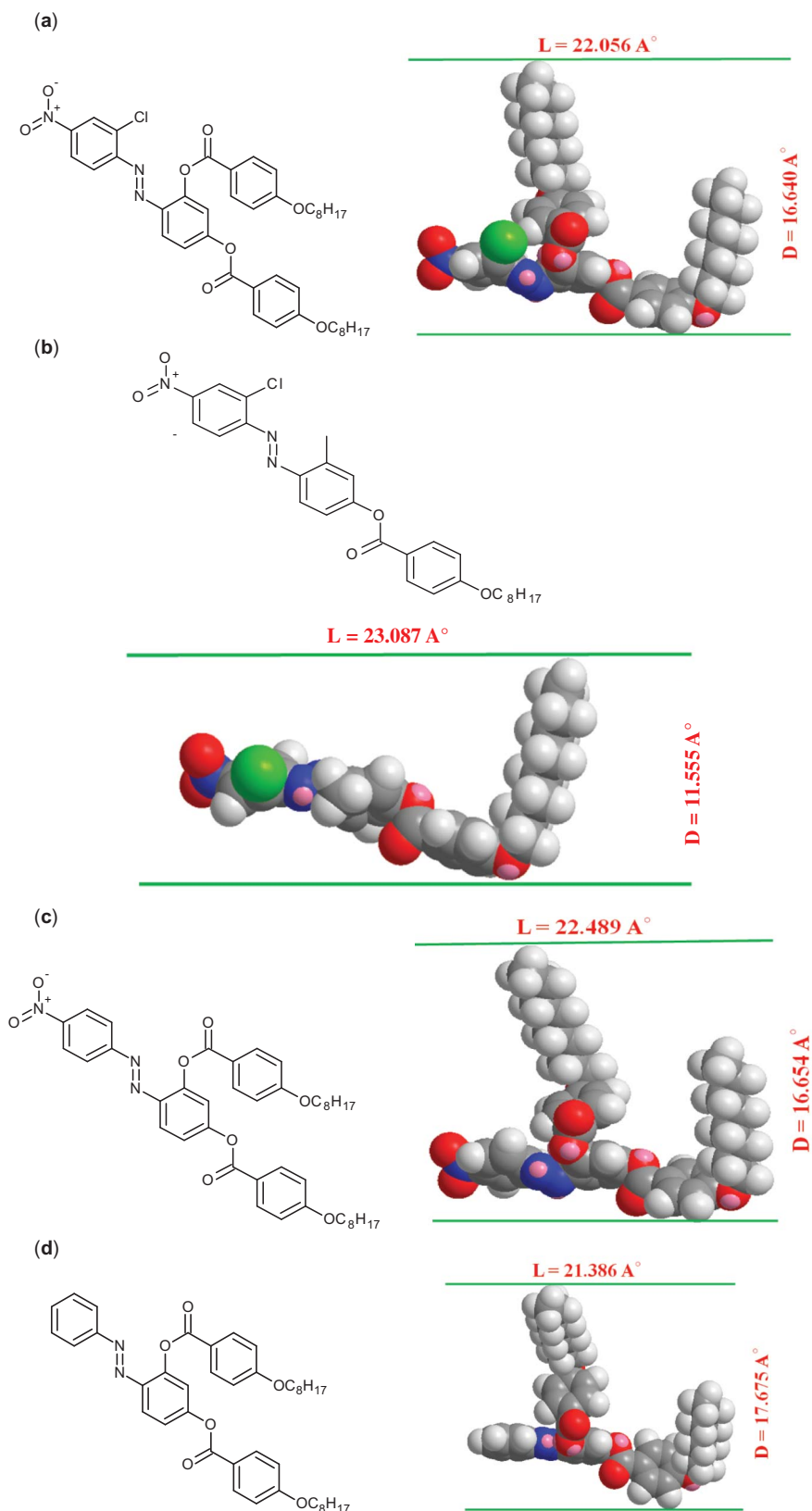
(a)

(b)

(c)

(d)

Figure 4. Transition temperatures, molecular structure and dimensions of compound **I–8** and structurally related compounds **II**, **III** and **IV**: compounds **I–8**: Cr (81°C) SmA 139°C, Iso; compound **II**: Cr (99°C N) 145°C, Iso; compound **III**: Cr (71°C) SmA 112°C, Iso; compound **IV**: Cr (88°C N) 101°C, Iso (colour version online).
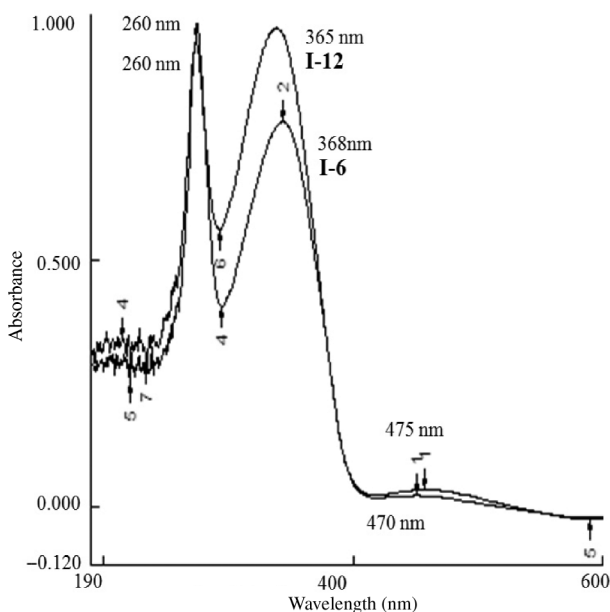
Figure 5. UV–Vis spectra of *n*-hexyloxy **(I–6)** and *n*-dodecyloxy **(I–12)** derivatives.

In the present series the lower members are non-mesogenic, the middle members monotropic nematic, and the higher members exhibit a smectic mesophase character. The presence of polar nitro- and chloro-substituents in these λ-shaped compounds induces smectogenic tendencies. The study has also indicated that the compounds of series **I–n** exhibit a nematic phase as well as a smectic A phase, with good mesophase range and higher thermal stability due to the presence of polar nitro- and chloro-groups.

Acknowledgements

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