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Self-assembly of azo molecules to mesogenic phasmid-like materials through inter-molecular hydrogen bonding

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A series of acid-functionalised new azo compounds was synthesised and characterised. The constituent molecules self-organise to form dimers through inter-molecular hydrogen bonding, resulting in phasmid-like compounds. This was once considered to be a promising molecular architecture to form biaxial nematic phases. The mesomorphic properties of these new azo compounds were studied using polarising optical microscopy, differential scanning calorimetry and X-ray diffraction. Investigations revealed that these compounds form nematic and columnar mesophases. A few more compounds were synthesised by replacing the –N=N- linkage in these compounds with –CH=N- and –COO- to study the effect of different linkages on the mesomorphic properties in such molecular systems. All were found to be liquid crystalline. The compounds with a –N=N- linkage are more conducive to mesomorphism and are thermally very stable. The effect of number of alkoxy chains on the mesomorphic properties of this system was also studied. To the best of our knowledge, at present, only a handful of phasmid-like mesogenic compounds, formed by the intermolecular hydrogen bonding, are known.

Keywords: azo compound; phasmid; hydrogen bonding; nematic phase; columnar phase

1. Introduction

Molecular architecture is an important factor that determines the liquid crystalline properties of a compound [1]. Several new molecular architectures have emerged in the recent past, forming exotic liquid crystalline materials that are of interest both from a fundamental and an application point of view [2–5]. There are several ways by which the molecular architecture of a compound can be changed relatively easily, for example, by forming metal complexes, charge transfer complexes, hydrogen-bonded compounds, etc. [1, 5, 6], which in many cases may lead to different and more interesting types of liquid crystalline materials than their respective parent compounds when compared with the conventional way of designing and synthesising new compounds consisting of covalent bonds.

The crucial role of hydrogen bonding in inducing and/or stabilising the liquid crystalline properties has long been recognised in certain systems. An early and classic example is that of the alkoxy benzoic acids [7, 8], wherein dimerisation of the molecules imparts enhanced structural anisotropy, which is a paramount factor for a compound to exhibit liquid crystalline properties. Hydrogen bonding has also been utilised for the preparation of a wide variety of self-assembled systems [5, 9–11]. These non-conventional approaches have led to the development of new self-organised functional materials exhibiting liquid crystalline properties.

As a part of our work on thermotropic biaxial nematic materials [12], it was decided to make a detailed investigation on other molecular architectures, which may form a biaxial nematic phase, other than the bent-core materials. In this direction, a new series of azo compounds and some of their azomethine and ester counterparts with carboxylic acid functional group were designed and synthesised. The molecules here self-assemble to form dimers through inter-molecular hydrogen bonding, resulting in phasmid-like compounds. This type of structure was once held to be a promising molecular architecture for the formation of biaxial nematic phases [13, 14]. As the constituent molecules of the compounds studied here clearly indicate a high molecular shape biaxiality [13, 14], one would expect a biaxial nematic phase to be exhibited by these compounds. However, later extensive experimental and deuterium nuclear magnetic resonance (NMR) studies on these compounds showed that the nematic phase exhibited by them is uniaxial in nature [15].

The molecular structures of the acid, that is, functionalised azo compounds and their azomethine and ester counterparts, synthesised in the present study are shown in Figure 1. The mechanism of self-organisation of the functionalised molecules through hydrogen bonding was employed to obtain the phasmid-like compounds of interest here. To the best of our knowledge, until the present, only a handful of phasmid-like mesogenic compounds, formed by intermolecular

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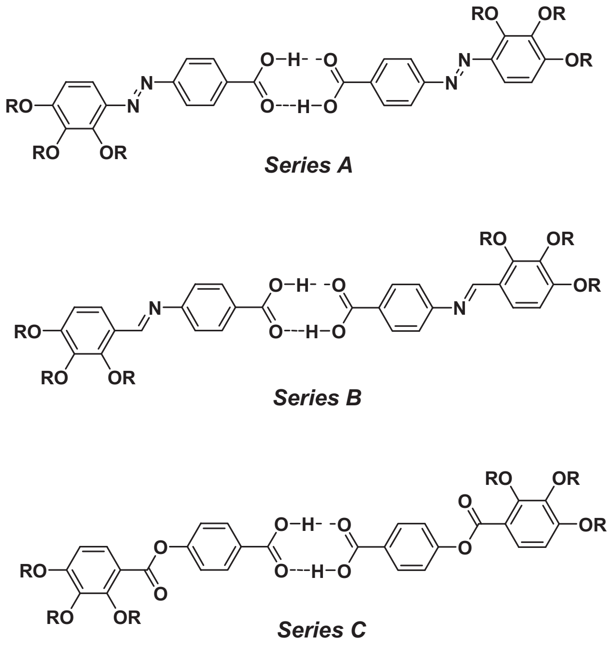


Figure 1. The molecular structures of the acid-functionalised new azo compounds (***Series A***) and their azomethine (***Series B***) and ester (***Series C***) counterparts.

hydrogen bonding, are known [5]. The presence of an azo linkage, which induces photochromism to the system in addition to the liquid crystalline properties, makes these compounds multifunctional and this potential may be exploited for application purposes.

2. Experimental

2.1 Synthesis

The compounds in the present study were obtained following the synthesis route shown in Scheme 1. Analytical reagent grade quality chemicals and solvents were obtained and the solvents dried using standard methods as and when required. The purity and the chemical structures of all the compounds synthesised were confirmed by spectral data. Infrared (IR) spectra were recorded using a Perkin-Elmer 1000 spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ on a 400 MHz Bruker NMR spectrometer, using Me_4Si as an internal standard. Microanalyses were performed using a Eurovector Elemental Analyser, Model Euro EA 3000.

2.1.1 *Ethyl 4-(2,3,4-Trialkoxyphenylazo)benzoate* (**2**)

The compound ***1***, synthesised following a procedure similar to one described earlier [16], was O-alkylated using an n-alkyl bromide. Thus, a catalytic amount of potassium iodide was added to a mixture of compound ***1*** (0.0066 mol), n-alkyl bromide (0.033mol) and K_2CO_3 (0.033 mol), in dry dimethylformamide (DMF) under anhydrous conditions. This was heated at 90°C for 12 h. The reaction mixture was then cooled to room temperature and poured into ice-cold water. The product was extracted with dichloromethane, washed with distilled water and dried over anhydrous sodium sulphate. The crude product obtained by removing the solvent, was purified by column chromatography. Yields varied between 40% and 60% for different homologues. The compound ***2*** was finally purified by recrystallisation using acetone. The spectral data obtained for all the homologues agreed very well with their chemical structures and the analytical data for one of the homologues with chain length $–OC_8H_{17}$, which is a very viscous and dark red coloured liquid at ambient temperature, are as follows:

IR (KBr): 2926, 2855, 1721, 1583, 1467, 1272, 1095 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.17 (d, $J = 8$ Hz, 2H, ArH), 7.92 (d, $J = 8$ Hz, 2H, ArH), 7.52 (d, $J = 9.16$ Hz, 1H, ArH), 6.71 (d, $J = 9.2$ Hz, 1H, ArH), 4.41 (q, $J = 7.12$ Hz, 2H, $–CO_2CH_2–$), 4.24 (t, $J = 6$ Hz, 2H, $–OCH_2–$), 4.0 (m, 4H, $–OCH_2–$), 1.26–1.87 (m, 39H, $–CH_2–$ and $–CO_2CH_2\underline{CH_3}–$), 0.93–0.84 (m, 9H, $–CH_3$).

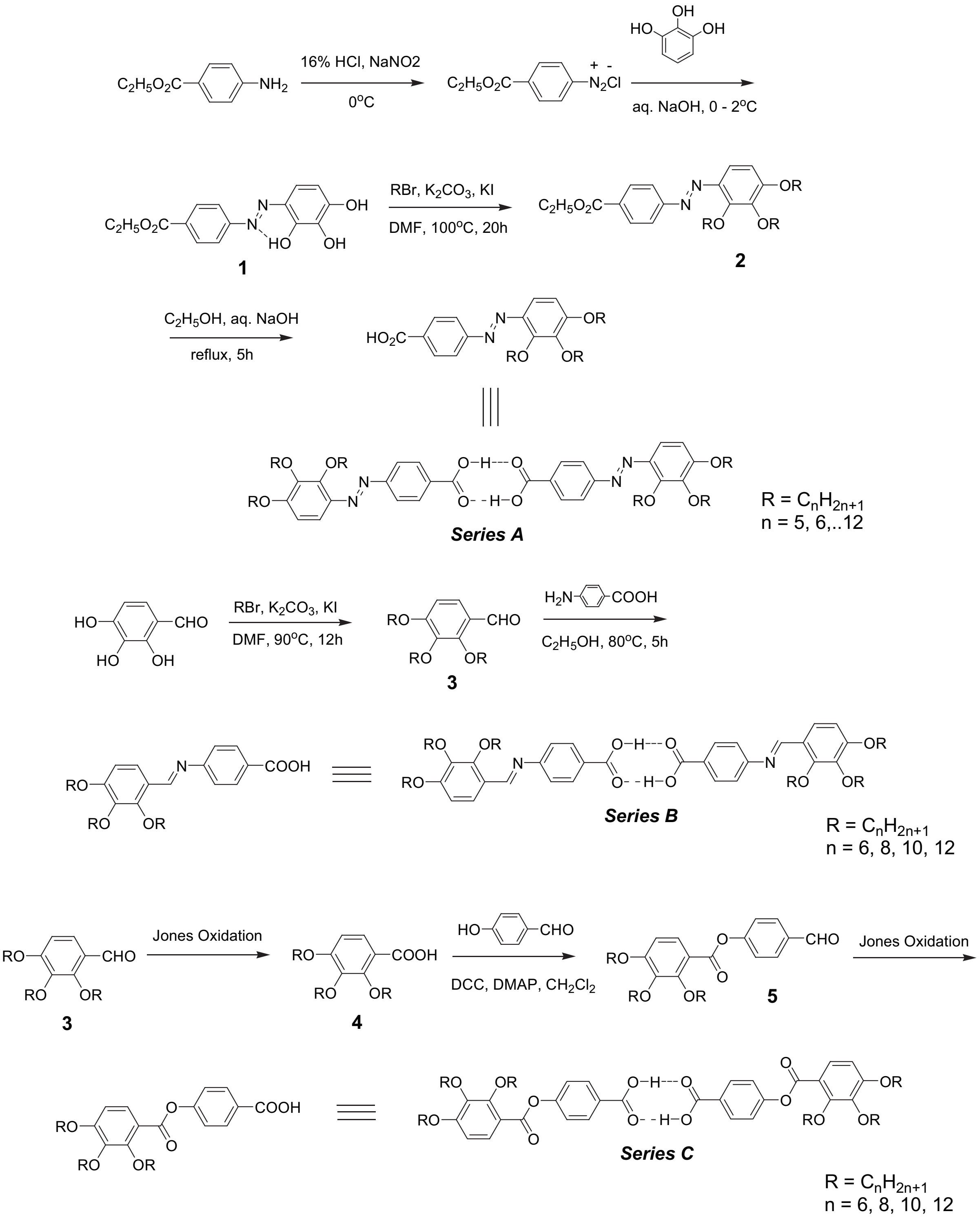
2.1.2 *4-(2,3,4-Trialkoxyphenylazo)benzoic acid* (**Series A**)

The compound ***2*** was subjected to hydrolysis under the basic conditions described earlier [16]. The product obtained was purified by recrystallisation, using either methanol or ethanol as required. Yields varied between 60% and 70% for different homologues. The analytical data obtained for all the homologues of ***Series A***, matched very well with their respective chemical structures. The data for one of the representative compound, with chain length $–OC_8H_{17}$ (***A-8***) are as follows:

IR (KBr): 2925, 2853, 1687, 1581, 1465, 1286, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.17 (d, $J = 8$ Hz, 2H, ArH), 7.89 (d, $J = 8$ Hz, 2H, ArH), 7.4 (d, $J = 9.2$ Hz, 1H, ArH), 6.6 (d, $J = 9.2$ Hz, 1H, ArH), 4.2 (t, $J = 6$ Hz, 2H, $–OCH_2–$), 4 (t, $J = 6$Hz, 4H, $Ar–OCH_2–$), 1.19–1.81 (m, 36H, $–CH_2–$), 0.78–0.84 (m, 9H, $–CH_3$). Elemental analysis calculated for $C_{37}H_{58}N_2O_5$, C 72.75, H 9.57, N 4.59; found, C 72.66, H 9.52, N 4.58.

2.1.3 *2,3,4-Trialkoxybenzaldehyde* (**3**)

To a solution of 2,3,4-trihydroxybenzaldehyde (0.003mol) in 10 ml dry DMF, was added K_2CO_3 (0.0162 mol), n-bromoalkane (0.0145 mol) and



Scheme 1. Synthetic route followed to obtain the new compounds of ***Series A***, ***B*** and ***C***.

catalytic amount of potassium iodide. The reaction mixture was heated while stirring for 12 h at 90°C. This was then cooled to room temperature and poured into ice-cold water (50 ml). The product was extracted with ether, washed with distilled water and dried over anhydrous sodium sulphate. The crude product was purified by column chromatography. The product was a very pale yellow coloured liquid with a yield of about 83%. The data obtained for the compound with chain length $–OC_{10}H_{21}$ are as follows:

IR (KBr): 2924, 2854, 2739, 1682, 1587, 1466, 1290, 1091 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 10.25 (s, 1H, –CHO), 7.57 (d, J = 8 Hz, 1H, ArH), 6.72 (d, J = 8 Hz, 1H, ArH), 4.18 (t, J = 6 Hz, 2H, $–OCH_2–$), 4.05 (t, J = 6 Hz, 2H, $–OCH_2–$), 3.99 (t, J = 6 Hz, 2H, $–OCH_2–$), 1.27–1.87 (m, 48H, $–CH_2–$), 0.86–0.90 (m, 9H, $–CH_3$).

2.1.4 *4-(2,3,4-trialkoxybenzylideneamino)benzoic acid* (Series B)

This compound was prepared following a procedure described earlier [17]. Yield was about 40%. The analytical data obtained for one of the compounds, with chain length $–OC_{10}H_{21}$ are as follows:

IR (KBr): 2921, 2851, 1684, 1585, 1467, 1290, 1167, 1091 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 8.73 (s, 1H, –CH=N–), 8.13 (d, J = 8 Hz, 2H, ArH), 7.86 (d, J = 8 Hz, 1H, ArH), 7.22 (d, J = 8 Hz, 2H, ArH), 6.76 (d, J = 8 Hz, 1H, ArH), 4.14 (t, J = 6, 2H, $–OCH_2–$), 4.06 (t, J = 6 Hz, 2H, $–OCH_2–$), 4.00 (t, J = 6 Hz, 2H, $–OCH_2–$), 1.24–1.87 (m, 48H, $–CH_2–$), 0.87 (m, 9H, $–CH_3$). Elemental analysis calculated for $C_{44}H_{71}NO_5$, C 76.14, H 10.31, N 2.02; found, C 76.06, H 10.28, N 2.09.

2.1.5 *2,3,4-Trialkoxybenzoic acid* (4)

This was prepared from ***3*** using Jones oxidation method described earlier [3, 4]. Yield was about 73%. The analytical data obtained for the compound with chain length $–OC_{10}H_{21}$ are as follows:

IR (KBr): 2920, 2851, 1692, 1593, 1465, 1287, 1099 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 11.35 (s, 1H, –COOH), 7.87 (d, J = 8 Hz, 1H, ArH), 6.78 (d, J = 8 Hz, 1H, ArH), 4.34 (t, J = 7 Hz, 2H, $–OCH_2–$), 4.05 (t, J = 6 Hz, 2H, $–OCH_2–$), 3.98 (t, J = 6 Hz, 2H, $–OCH_2–$), 1.27–1.86 (m, 48H, $–CH_2–$), 0.88 (m, 9H, $–CH_3$).

2.1.6 *4-Formylphenyl 2,3,4-trialkoxybenzoate* (5)

This compound was prepared by the esterification of ***4*** with 4-hydroxybenzaldehyde using the DCC coupling method described earlier [3, 4, 17]. The product was recrystallised using methanol. Yield was about 45%. The analytical data obtained for one of the compounds with chain length $–OC_{10}H_{21}$ are as follows:

IR (KBr): 2926, 2857, 2739, 1745, 1703, 1590, 1452, 1286, 1206, 1118, 1085 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 10.01 (s, 1H, –CHO), 7.96 (d, J = 8 Hz, 2H, ArH), 7.77 (d, J = 8 Hz, 1H, ArH), 7.39 (d, J = 8 Hz, 2H, ArH), 6.74 (d, J = 8 Hz, 1H, ArH), 4.13 (t, J = 6Hz, 2H, $–OCH_2–$), 4.06 (t, J = 6Hz, 2H, $–OCH_2–$), 4.00 (t, J = 6Hz, 2H, $–OCH_2–$), 1.23–1.87 (m, 48H, $–CH_2–$), 0.88 (m, 9H, $–CH_3$).

2.1.7 *4-(2,3,4-Tridecyloxybenzoyloxy)benzoic acid* (Series C)

This compound was obtained by the Jones oxidation of compound ***5***. The product was recrystallised using methanol and the yield was about 70%. The analytical data obtained for one of the compounds with chain length $–C_{10}H_{21}$ are as follows:

IR (KBr): 2952, 2922, 2851, 1741, 1686, 1592, 1288, 1208, 1118, 1012 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 8.18 (d, J = 8 Hz, 2H, ArH), 7.77 (d, J = 8 Hz, 1H, ArH), 7.32 (d, J = 8 Hz, 2H, ArH), 6.73 (d, J = 9 Hz, 1H, ArH), 4.13 (t, J = 6 Hz, 2H, $–OCH_2–$), 4.06 (t, J = 6 Hz, 2H, $–OCH_2–$), 4.01 (t, J = 6Hz, 2H, $–OCH_2–$), 1.86–1.23 (m, 48H, $–CH_2–$), 0.90–0.85 (m, 9H, $–CH_3$). Elemental analysis calculated for $C_{44}H_{70}O_7$, C 74.33, H 9.92; found, C 74.46, H 9.91.

2.1.8 *4-(3,4-dialkoxyphenylazo)benzoic acid* (Series E)

This compound was prepared following a similar procedure as for ***Series A***. The analytical data for one of the representative compounds, with chain length $–OC_{10}H_{21}$ (***E-10***) are as follows:

IR (KBr): 2918, 2849, 1680, 1586, 1504, 1463, 1423, 1266 and 1113 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, J = 8.4 Hz, 2H, ArH), 7.94 (d, J = 8.6 Hz, 2H, ArH), 7.65–7.63 (m, 1H, ArH), 7.51 (d, J = 2.3 Hz, 1H, ArH), 7.0 (d, J = 8.5 Hz, 1H, ArH), 4.1 (m, 4H, Ar-$OCH_2–$), 1.89–1.22 (m, 32H, $–CH_2–$), 0.88 (m, 6H, $–CH_3$); Elemental analysis calculated for $C_{33}H_{50}N_2O_4$, C73.57, H 9.35, N 5.2; found, C 73.88, H 9.27, N 4.89.

2.2 *Mesophase characterisation*

The microscopic textural observations were made using an Olympus BX51 polarising optical microscope (POM) in conjunction with a Mettler FP82HT hot stage. The exact temperatures of phase transitions and the associated enthalpies were determined by differential scanning calorimetric (DSC) scans obtained from the Perkin Elmer DSC-Diamond series. The heating and cooling rates were 10°C min^{-1}.

X-ray studies were performed at the Advanced Photon Source of Argonne National Laboratory, using the Midwestern Universities Collaborative Team's beamline on sector 6. An X-ray wavelength of 0.7653 Å was used. The diffraction patterns were collected using a high resolution MAR345 area detector placed at a distance of 518.5 mm from the sample. The sample temperature was controllable with a precision of ± 1°C, using a home-made oven and temperature controller. The 2θ scans were generated from the two-dimensional diffraction patterns using the software package FIT2D developed by A.P. Hammersley of the European Synchrotron Radiation Facility [18].

3. Results and discussion

3.1 Phase behaviour

In the present study a series of new azo carboxylic acids, ***Series A*** and a few of their azomethine (***Series B***) and ester (***Series C***) counterparts were synthesised, which self-organise through inter-molecular hydrogen bonding to form dimers. These dimers possess a phasmid-like structure, which was once considered to be a very promising molecular architecture for the formation of biaxial nematic phases [13,14]. Almost all the compounds synthesised here exhibit liquid crystalline phases. They exhibit nematic and columnar mesophases. The thermal behaviour of all these compounds was investigated using POM and DSC. The transition temperatures (°C) and the enthalpies of different transitions (kJ mol^{-1}) obtained from the DSC thermograms are given in Table 1. In ***Series A***, we synthesised eight new azo compounds starting from the chain length, $-OC_5H_{11}$ (***A-5***) to $-OC_{12}H_{25}$ (***A-12***). As can be seen from Table 1, the compound ***A-5*** is non-mesopmorphic. As the chain length was increased, the mesomorphism was induced in compound ***A-6*** onwards. ***A-6*** exhibits a monotropic nematic and columnar mesophases.

Ascending along the series from ***A-7*** to ***A-10***, the nematic phase becomes enantiotropic whereas the columnar phase remains as a monotropic phase throughout the series. Once again both these phases become monotropic in the case of the higher homologues ***A-11*** and ***A-12***. Many of these compounds exhibit crystal to crystal transitions in addition to mesomorphism. It can be seen from Table 1 that all the homologues of ***Series A*** have fairly low transition temperatures, with ***A-6*** having the highest clearing temperature (134°C) in this series. We found that the compound ***A-8*** has the widest mesophase range. The POM textures observed for the nematic and columnar mesophases of the compound ***A-8*** are shown in Figure 2. The typical Schlieren texture for the nematic phase of these compounds could not be obtained. They always showed a marble-like texture with a few two-brush patterns in some regions. A homeotropic configuration for the nematic phase of these compounds could not be obtained by any conventional methods. The preliminary optical studies in the nematic phase of ***A-8***, revealed some kind of peculiarity of this mesophase, which was also reflected in their X-ray diffraction patterns.

As mentioned earlier, we synthesised some of azomethine (***Series B***) and ester (***Series C***) counterparts of ***Series A*** to study the effect of different linkage groups on the mesomorphic behaviour in such molecular architecture. We found that the compounds of both ***Series B*** and ***C***, exhibit a nematic mesomorphism. The thermal data for these two series are given in Tables 2 and 3, respectively. The thermal stabilities of the compounds and their mesophases of ***Series A***, ***B*** and ***C***, were studied both by POM and DSC investigations. The compounds of ***Series A*** with azo linkage were found to be more conducive to mesomorphism and were thermally very stable as confirmed by the DSC thermograms shown in Figure 3. Although the transition temperatures of azomethine compounds (***Series B***) are slightly lower than that of ***Series A***, they were found to be thermally somewhat unstable.

Table 1. Transition temperatures (°C) and enthalpies of transitions (kJ mol^{-1}) for the compounds of ***Series A***.

Compound	R	First heating	First cooling
A-5	C_5H_{11}	**Cr** 160.0 (33.47) **Iso.**	**Iso.** 154.0 (*31.49*) **Cr**
A-6*	C_6H_{13}	**Cr** 134.1 (*24.80*) **Iso.**	**Iso.** 133.9 (*1.21*) **N** 122.9 (*8.11*) **Col**$_h$ 118.6 (*5.49*) **Cr**
A-7 *	C_7H_{15}	**Cr** 112.0 (*25.80*) **N** 127.4 (*0.97*) **Iso.**	**Iso.** 125.9 (*0.98*) **N** 107.9 (*6.55*) **Col**$_h$ 97.5 (*1.23*) **Cr**
A-8	C_8H_{17}	**Cr** 106.9 (*26.84*) **N** 124.0 (*0.66*) **Iso.**	**Iso.** 122.9 (*0.73*) **N** 96.3 (*3.38*) **Col**$_h$ 84.0 (*19.26*) **Cr**
A-9*	C_9H_{19}	**Cr** 108.2 (*35.52*) **N** 118.5 (*0.55*) **Iso.**	**Iso.** 117.3 (*0.73*) **N** 90.5 (*2.17*) **Col**$_h$ 86.7 (*27.28*) **Cr**
A-10*	$C_{10}H_{21}$	**Cr** 106.5 (*38.58*) **N** 115.5 (*0.64*) **Iso.**	**Iso.** 114.9 (*0.72*) **N** 92.9 (2.37) **Col**$_h$ 85.5 (*31.74*) **Cr**
A-11*	$C_{11}H_{23}$	**Cr** 107.0 (*46.28*) **Iso.**	**Iso.** 106.1 (*0.59*) **N** 88.2 (*1.27*) **Col**$_h$ 84.4 (*37.25*) **Cr**
A-12*	$C_{12}H_{25}$	**Cr** 106.2 (*48.49*) **Iso.**	**Iso.** 104.30 (*0.62*) **N** 90.5 (1.98) **Col**$_h$ 82.9 (*43.63*) **Cr**

*These compounds exhibit Cr–Cr transitions.

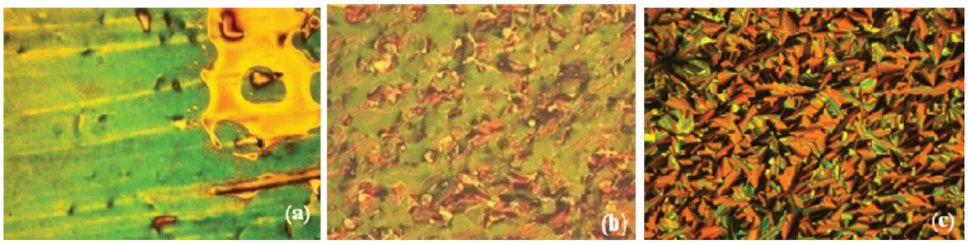


Figure 2. Polarising optical microscope textures of (a) nematic at 120°C, (b) nematic to columnar at 96°C and (c) columnar at 94°C mesophases exhibited by the compound ***A-8***.

Table 2. Transition temperatures (°C) and enthalpies of transitions (kJ mol^{-1}) for the compounds of ***Series B***.

Compound	R	First heating	First cooling
B-6	C_6H_{13}	**Cr** 140.3 (*31.17*) **Iso.**	**Iso.** 135.2 (*28.94*) **Cr**
B-8	C_8H_{17}	**Cr** 110.4 (*22.43*) **Iso.**	**Iso.** 104.7* **N** 102.4 (*9.62*) **Cr**
B-10	$C_{10}H_{21}$	**Cr** 86.7 (*39.18*) **N** 98.1 (*1.04*) **Iso.**	**Iso.** 97.2 (*0.89*) **N** 77.5 (*17.43*) **Cr**
B-12	$C_{12}H_{25}$	**Cr** 91.2 (*48.09*) **N** 94.9 (0.*19*) **Iso.**	**Iso.** 91.6 (*0.69*) **N** 72.8 (*49.37*) **Cr**

*Enthalpy could not be measured due to the onset of crystallisation.

Table 3. Transition temperatures (°C) and enthalpies of transitions (kJ mol^{-1}) for the compounds of ***Series C***.

Compound	R	First heating	First cooling
C-6	C_6H_{13}	**Cr** 121.1 (*25.86*) **Iso.**	**Iso.** 117.1 (*25.18*) **Cr**
C-8	C_8H_{17}	**Cr** 107.2 (*22.57*) **Iso.**	**Iso.** 103.7 (*21.90*) **Cr**
C-10	$C_{10}H_{21}$	**Cr** 89.5 (*39.48*) **N** 92.3 (*0.59*) **Iso.**	**Iso.** 91.4 (0.*75*) **N** 77.0 (*17.11*) **Cr**
C-12	$C_{12}H_{25}$	**Cr** 93.4 (*56.59*) **Iso.**	**Iso.** 86.0 (*0.70*) **N** 71.3 (*10.17*) **Cr**

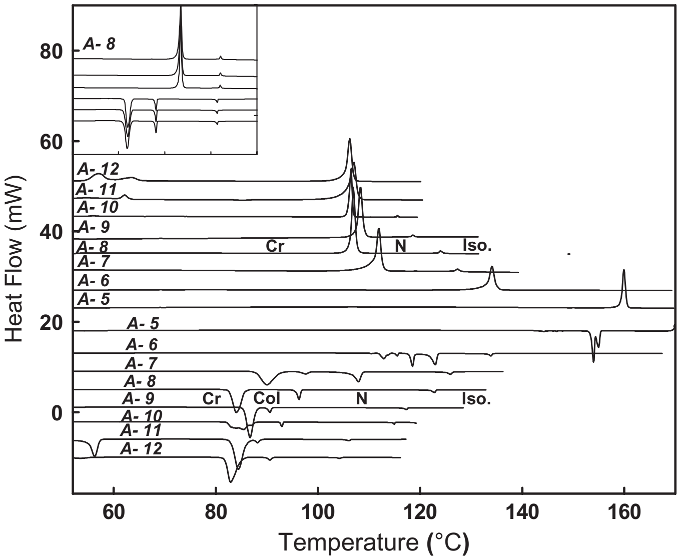
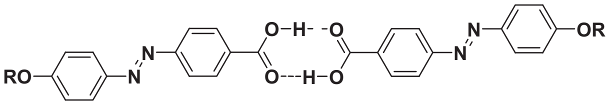
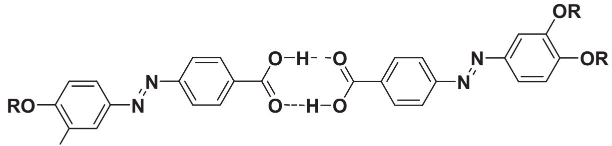


Figure 3. Differential scanning calorimetry scans for the compounds of ***Series A***. The inset shows the reproducibility of the transition temperatures on three consecutive heating and cooling cycles of one of the compounds, ***A-8***.



Series D



Series E

Figure 4. The molecular structures of ***Series D*** and ***E***.

Also, they were found to be less conducive to mesomorphism when compared with azo compounds of ***Series A***. The compounds of ***Series C*** with ester linkage were the least conducive to mesomorphism and they exhibited mesophases only for a very short range.

We intended to study the effect of the number of alkoxy chains present in the dimers on the mesomorphic properties of compounds of ***Series A***. The compounds with just one alkoxy chain on each side of the dimers, ***Series D*** (Figure 4), are known in the literature [16, 19]. These compounds exhibit nematic and smectic mesophases. The compounds, with two alkoxy chains on either side of the dimers, ***Series E*** (Figure 4), were not known in the literature. So, these compounds were synthesised in our laboratory. The thermal data for these compounds are given in Table 4. Surprisingly, they were found to be the least conducive to mesomorphism. However, as seen already, that when there are three alkoxy chains on each end of the dimers (***Series A***), they exhibit nematic and columnar mesophases for a fairly wide temperature range. It is not clear at this juncture why the compounds of ***Series E*** are the least conducive to mesomorphism. Similar compounds with ester linkage with only two alkoxy chains on each end of the molecules have also been found to be less conducive to mesomorphism [20].

The hydrogen-bonded phasmid-like compounds reported by Praefcke *et al.* [14] are the dimers of cinnamic acids consisting of only two phenyl rings in the dimer structure. They exhibited only a monotropic nematic mesophase. Whereas in our compounds (***Series A***), the dimers have four phenyl rings and exhibit both nematic (enantiotropic in some cases) and columnar mesophases. Thus, these compounds represent a hybrid class of both calamitic and discotic liquid crystals.

3.2 X-ray studies

For X-ray diffraction measurements, the compounds were loaded into 1.0 mm diameter Lindéman capillaries with 10 μm thick walls and placed in a home-made oven. The data were calibrated against a silicon standard (NIST 640C). The intensity of the incident beam was controlled using a bank of Cu and Al attenuators.

For the compound ***A-8***, the isotropic phase was reached at 124°C as confirmed by two diffuse rings in the diffraction pattern. In the nematic phase, diffraction peaks exhibit diffuse character, indicating a liquid-like nature and lack of any long-range positional order at this temperature. It should be mentioned here that we obtained unconventional X-ray diffraction patterns in the nematic range of this compound. This pattern was quite different from the typical X-ray scattering pattern of the aligned nematic phase, which presumably originates from a structure of the dimer. However, at this juncture, it is too difficult to confirm a precise structure for the dimer that is formed by inter-molecular hydrogen bond. To understand and interpret the results more accurately in the present case, a more detailed X-ray diffraction and other physical studies on this compound need to be performed. Below the transition point to columnar phase at 96.2°C, the small angle peak condenses and dramatically sharpens while the large angle peak remains essentially unchanged, as seen in Figures 5(a) and (b), indicating the establishment of one dimensional positional order along the short axis of the columns. The corresponding graph in Figure 5 shows that the small angle peak (24.6 Å) is significantly condensed while the large angle peak (4.5 Å) is liquid-like. In addition, the second (14.2 Å) and

Table 4. Transition temperatures (°C) and enthalpies of transitions (kJ mol^{-1}) for the compounds of ***Series E***.

Compound	R	First heating	First cooling
E-9	C_9H_{19}	**Cr** 158.1 (*48.6*) **Iso.**	**Iso.** 151.2 (*44.4*) **Cr**
E-10	$C_{10}H_{21}$	**Cr** 148.7 (*28.5*) **Iso.**	**Iso.** 141.1 (*47.5*) **Cr**
E-12	$C_{12}H_{25}$	**Cr** 145.5 (*46.0*) **Iso.**	**Iso.** 141.0* **N** 140.0 (*50.0*) **Cr**
E-14	$C_{14}H_{29}$	**Cr** 143.8 (*52.8*) **Iso.**	**Iso.** 138.7 (*13.4*) **Cr**

*Enthalpy could not be measured due to the onset of crystallisation.

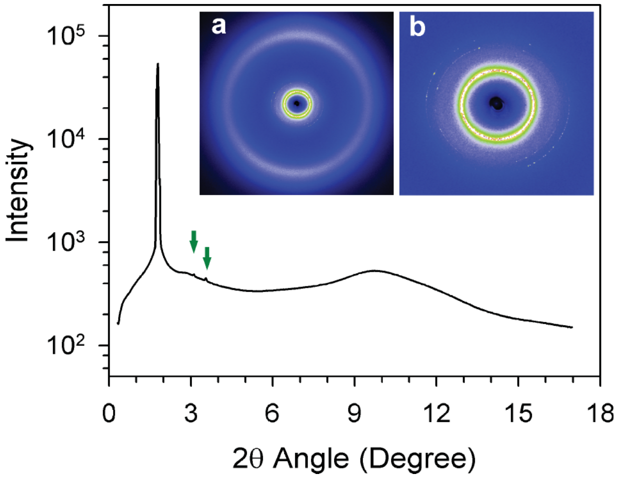


Figure 5. X-ray diffraction pattern of the hexagonal columnar liquid crystal ($\mathrm{Col_h}$) phase obtained from the compound ***A-8*** at 93°C. (a) and (b) represent wide and small angle diffraction patterns, respectively, at the corresponding temperature.

third (12.3 Å) peaks, marked by arrows, at a small angle confirm the hexagonal order of the columns. Therefore, this phase clearly represents a hexagonal columnar liquid crystal phase at this temperature. Just below the columnar liquid crystal phase at 84.0°C, the sample adopts a crystalline structure as shown by the multiple sharp peaks at both small and large angles of diffraction.

4. Summary

We synthesised a series of azo carboxylic acids (***Series A***), which dimerise through inter-molecular hydrogen bonding, resulting in phasmid-like compounds. These dimers represent a hybrid class of calamitic and discotic liquid crystals. They exhibit nematic and columnar mesophases. X-ray studies confirmed the hexagonal nature of the columnar mesophase of these compounds. To elucidate the exact nature of the nematic phase, a detailed X-ray and other physical studies are in progress. The effect of molecular structure on the mesomorphic properties was also studied by changing the linkage group as well as by varying the number of alkoxy chains in ***Series A***. From the investigations, it was found that among the compounds synthesised here, the azo carboxylic acids of ***Series A*** are more conducive to mesomorphism and are thermally very stable, with a wide mesophase range and fairly low transition temperatures.

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