This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

**Liquid Crystals**

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

# Synthesis and studies of some 4-substituted phenyl-4'-azopyridine-containing hydrogen-bonded supramolecular mesogens

V. Ajay Mallia[a]; P. K. Sudhadevi Antharjanam[a]; Suresh Das[a]
[a] Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India,

Online publication date: 11 November 2010

**To cite this Article** Mallia, V. Ajay , Antharjanam, P. K. Sudhadevi and Das, Suresh(2003) 'Synthesis and studies of some 4-substituted phenyl-4'-azopyridine-containing hydrogen-bonded supramolecular mesogens', Liquid Crystals, 30: 2, 135 — 141

**To link to this Article: DOI:** 10.1080/0267829021000060214
**URL:** http://dx.doi.org/10.1080/0267829021000060214

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or 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.

LIQUID CRYSTALS, 2003, VOL. 30, NO. 2, 135–141

# Synthesis and studies of some 4-substituted phenyl-4′-azopyridine-containing hydrogen-bonded supramolecular mesogens

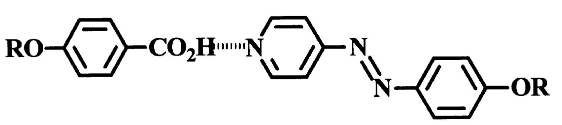
V. AJAY MALLIA, P. K. SUDHADEVI ANTHARJANAM and SURESH DAS*
Photochemistry Research Unit, Regional Research Laboratory (CSIR),
Trivandrum 695 019, India

(*Received 8 May 2002; in final form 23 September 2002; accepted 11 October 2002*)

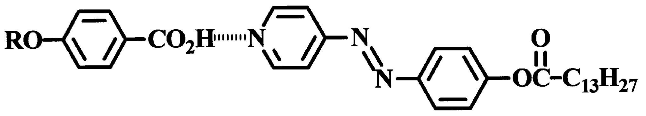
Novel azopyridine-containing supramolecular liquid crystalline (LC) materials built via 1 : 1-heterointermolecular hydrogen bonding between some 4-substituted phenyl-4′-azopyridines and 4-*n*-alkyloxybenzoic acids are reported. These hydrogen-bonded LC complexes exhibit well defined nematic, smectic A and smectic C phases over wide ranges of temperature depending upon the number of carbon atoms present in the alkyl chains. The formation of pure LC materials on 1 : 1-complexation could be confirmed from the phase diagrams of the binary mixtures, which clearly indicated a melting maximum for the 50 mol % mixture as well as the presence of two eutectic points on either side of this mixture.

## 1. Introduction

Supramolecular liquid crystals (LCs), obtained via intermolecular hydrogen bonding have attracted considerable attention during the last decade [1–21]. A number of such systems has been investigated following the reports of Kato and Frechet in 1989 [1, 2] and the subject has been extensively reviewed [9, 21]. Our interest in this area has been concerned with the design of photoactive hydrogen-bonded LCs using suitable hydrogen bond donors and acceptors [22–24]. Photoisomerization of azobenzene has been used to design photochromic liquid crystals, since the rod like *trans*-isomer of azobenzene is known to stabilize the LC phase, whereas the bent shaped *cis*-isomer is known to destabilize it [25–27]. Sequential UV and visible light photolysis of supramolecular hydrogen-bonded LC polymers containing azobenzene units has earlier been reported to bring about reversible nematic to isotropic phase transitions [14]. The aim of the present study has been to synthesize novel supramolecular hydrogen bonded mesogens bearing photoactive azopyridyl chromophores (schemes 1 & 2) and to study their LC and photoisomerization properties.



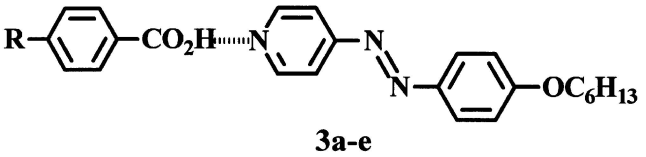
**1a-e**



**2a-e**

**a, R = $C_4H_9$**
**b, R = $C_6H_{13}$**
**c, R = $C_8H_{17}$**
**d, R = $C_{10}H_{21}$**
**e, R = $C_{12}H_{25}$**

Scheme 1.



**3a-e**

**a, R = H**
**b, R = Cl**
**c, R = $NO_2$**
**d, R = CN**

Scheme 2.

## 2. Results and discussion

### 2.1. *Syntheses*

4-Hydroxyphenyl-4′-azopyridine (HPAP) was synthesized by diazotization of 4-aminopyridine followed by coupling with phenol. Alkylation of HPAP by *n*-alkyl bromides in the presence of sodium hydroxide and

---

*Author for correspondence; e-mail: sdaas@rediffmail.com

*Liquid Crystals* ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829021000060214

*N*,*N*-dimethylformamide gave the 4-alkyloxyphenyl-4′-azopyridines (*n*-PAP, where *n* is the number of carbon atoms in the alkyl chain) in 60–70% yields. Reaction of *n*-tetradecanoic acid with thionyl chloride afforded the acid chloride ($C_{13}H_{27}COCl$), which on subsequent reaction with HPAP in dry dichloromethane and triethylamine gave 4-pyridylazo-4′-phenyl-*n*-tetradecanoate (72% yield). All the compounds were characterized on the basis of spectral data. Details are provided in the experimental section. The hydrogen-bonded assemblies (**1a**–**e** and **2a**–**e**) were synthesized by thoroughly mixing equimolar quantities of the hydrogen bond donors and hydrogen bond acceptors at temperatures above their melting points for a few minutes. The mixture was then allowed to cool slowly to yield the liquid crystalline materials. The formation of H-bonded LC complexes as shown in scheme 1, was confirmed by IR spectroscopic experiments. The IR spectra showed the characteristic stretching bands (two bands centred around 2500 and 1950 $cm^{-1}$) resulting from complexation of the carboxylic acid and pyridine through intermolecular hydrogen bonding [28, 29]. These bands replace the O–H band around 3000 $cm^{-1}$ observed for the weakly hydrogen-bonded acid dimers observed in the in the pure acid.

### 2.2. *Thermal properties*

The hydrogen bonded complexes (scheme 1) show enantiotropic LC behaviour as revealed by polarizing optical microscopy (POM). All the complexes behave as single mesogenic materials and show clear phase transitions which were reproducible over several heating and cooling cycles. The thermal properties of the complexes are different from those of the individual components. POM of **1a** revealed a nematic (N) LC phase. On cooling from the isotropic liquid, birefringent droplets were first observed, with final development of the schlieren texture, characteristic of a N phase, see figure 1 (*a*) [30]. The supramolecular assemblies **1b** and **1c** showed both smectic A (SmA) and N phases in the heating and cooling cycle, whereas for **1d** and **1e**, focal-conic textures (figure 1 (*b*) [30]) with homeotropic areas were observed, clearly confirming the formation of a SmA phase. The phase transition temperatures observed for **1a**–**e** are summarized in table 1. Figure 2 illustrates the dependence of the transition temperatures of the complexes on the chain lengths of the alkyl groups. With increasing chain length, smectic properties begin to appear, and the range of the nematic phase decreases with each increment in the alkyl chain, until in the decyloxy and dodecyloxy complexes, only the smectic phase is observed. The observed dependence of phase properties on alkyl chain length is similar to that reported for liquid crystalline molecules obtained via covalent linkage [31]. A similar dependence was also reported for the LCs generated *via* hydrogen bonding between bipyridyl and alkyloxybenzoic acids [32].

Table 1. Phase transition temperatures (°C) of **1a**–**e**: Cr = crystalline, N = nematic, SmA = smectic A and I = isotropic phase.

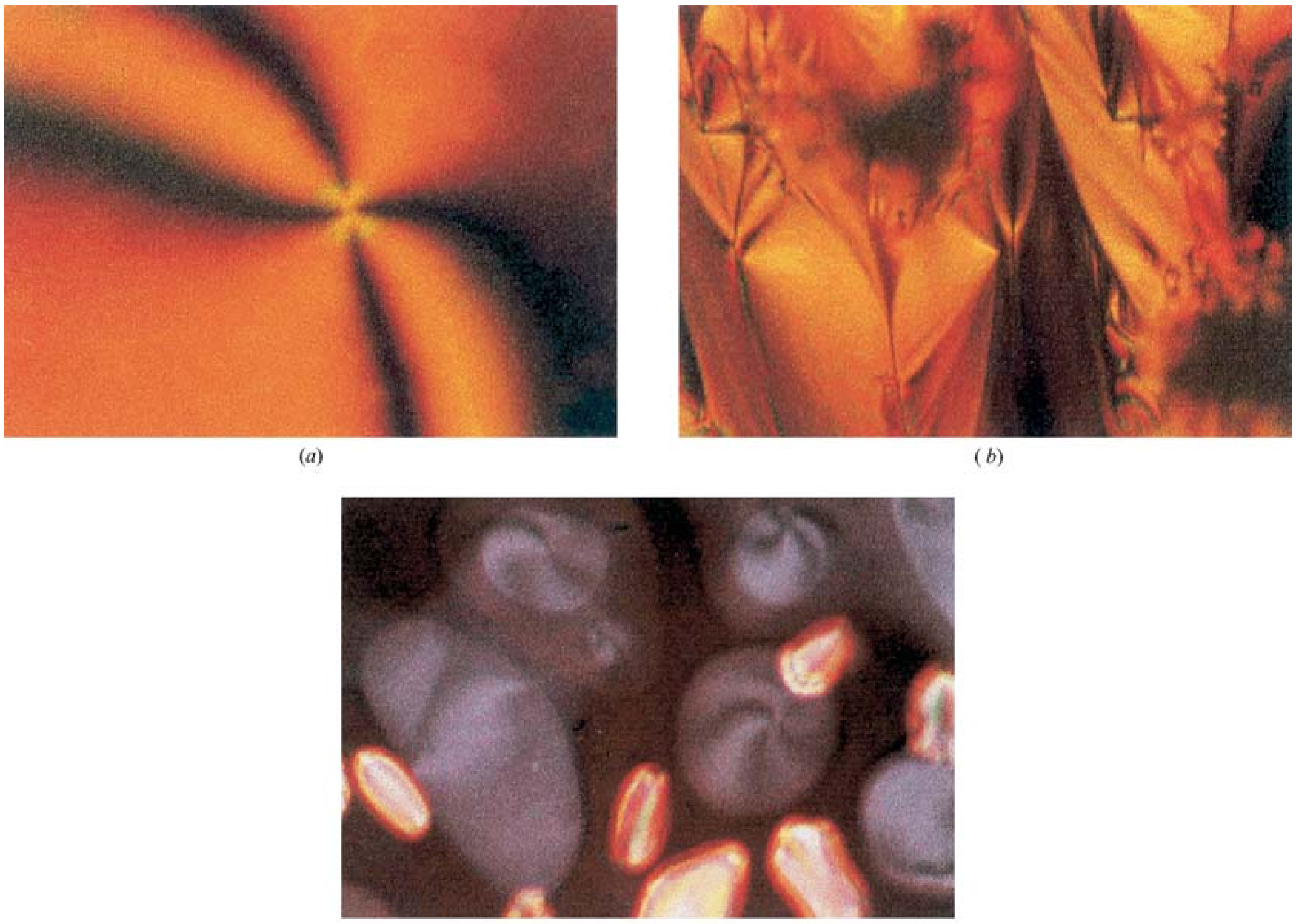
| Compound | Heating | Cooling |
|---|---|---|
| **1a** | Cr 110 N 143 I | I 135 N 100 Cr |
| **1b** | Cr 101 SmA 117 N 137 I | I 134 N 108 SmA 100 Cr |
| **1c** | Cr 104 SmA 123 N 131 I | I 130 N 121 SmA 101 Cr |
| **1d** | Cr 92 SmA 126 I | I 120 SmA 85 Cr |
| **1e** | Cr 100 SmA 131 I | I 128 SmA 91 Cr |

DSC curves obtained for the assemblies confirmed the number of LC phases observed by POM. The DSC thermogram obtained for **1d** is shown in figure 3. In the heating cycle, **1d** showed endotherms at 81°C due to a crystal (Cr) to crystal transition, at 97°C due to the Cr–SmA transition and at 125°C due to the SmA to isotropic phase transition.

Supramolecular hydrogen bonded assemblies **2a**–**e** were found to be smectogenic (table 2). The complex **2a** showed a fan-shaped texture, with homeotropic areas, which confirmed the formation of a SmA phase, whereas **2b** exhibited both SmA and SmC phases. On heating, **2b** first transformed into a blurred schlieren texture, characteristic of a SmC, which then became focal-conic with homeotropic areas characteristic of a SmA phase [30]. The hydrogen-bonded assemblies **2c**–**e** showed SmC phases. Upon cooling from the isotropic liquid, formation of bâtonnets which changed into four-brush schlieren textures clearly confirmed the formation of SmC phases in these assemblies, see figure 1 (*c*) [30]. With increasing length of the alkoxy chain, the SmC phase is favoured in the compounds **2a**–**e** (figure 4). A similar trend was observed for hydrogen-bonded assemblies reported earlier [32, 33]. In the assemblies **2a**–**e**, the clearing temperatures of the materials were almost independent of the chain length (figure 4).

Table 2. Phase transition temperatures (°C) of **2a**–**e**: Cr = crystalline, N = nematic, SmA = smectic A, SmC = smectic C and I = isotropic phase.

| Compound | Heating | Cooling |
|---|---|---|
| **2a** | Cr 76 SmA 125 I | I 123 SmA 50 Cr |
| **2b** | Cr 75 SmC 112 SmA 127 I | I 124 SmA 112 SmC 46 Cr |
| **2c** | Cr 76 SmC 129 I | I 126 SmC 45 Cr |
| **2d** | Cr 80 SmC 127 I | I 125 SmC 78 Cr |
| **2e** | Cr 84 SmC 129 I | I 127 SmC 82 Cr |


(*a*) (*b*)

(*c*)

Figure 1. Optical micrograph of (*a*) the nematic schlieren texture observed for **1a**, at 120°C in the cooling cycle, (*b*) focal-conic texture observed for **1e**, at 115°C in the cooling cycle, and (*c*) four-arm brushes and bâtonnets observed for the SmC phase of **2c**, at 123°C in the cooling cycle.

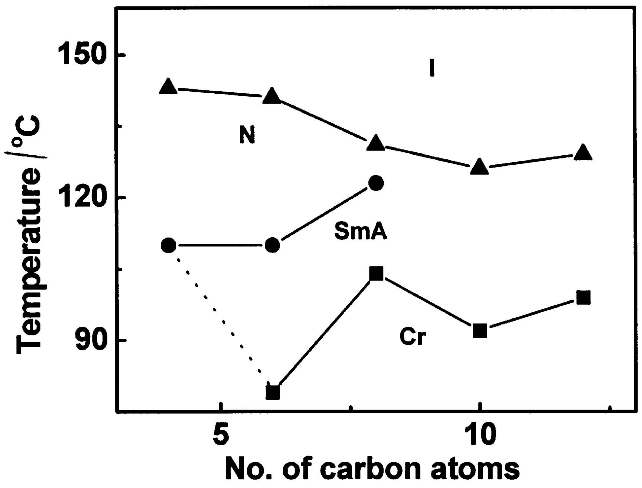


Figure 2. Plot of transition temperature against the number of carbon atoms ($n$) in the alkyl chain for the 1 : 1 hydrogen-bonded complexes, **1a**–**e**.

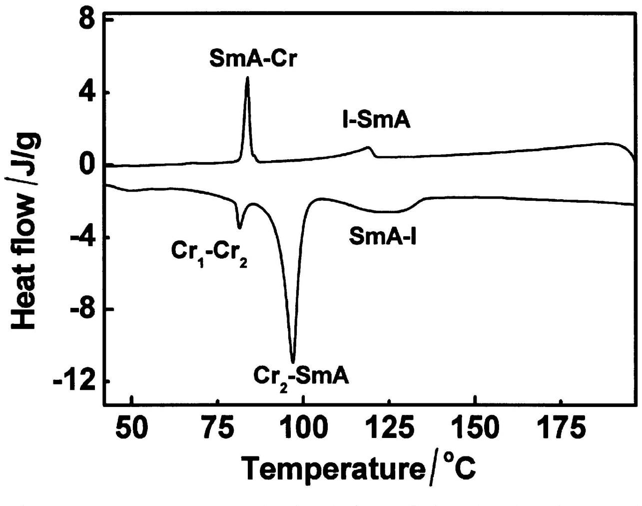


Figure 3. DSC trace obtained for **1d** in the heating and cooling cycles.

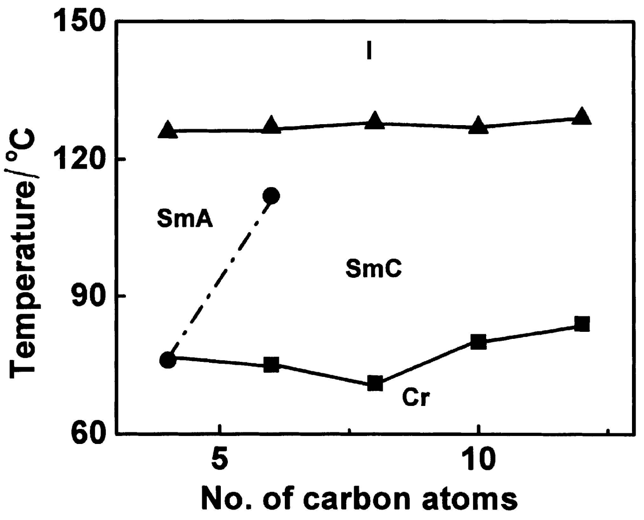


Figure 4. Plot of transition temperature against the number of carbon atoms ($n$) in the alkyl chain for the 1 : 1 hydrogen-bonded complexes, **2a**–**e**.

The LC properties of materials are highly dependent on substituents present in the molecules. In hydrogen-bonded LCs these properties can be related to the strength of the hydrogen bonds involved [12]. In the pyridine/acid complexes the association is primarily affected by the acidity of the H-donor and the basicity of the pyridine derivative. We have investigated the effect of substituents on the mesomorphic properties of the supramolecular assemblies formed between 4-hexyloxyphenyl-4′-azopyridine (6-PAP) and benzoic acid derivatives (scheme 2). The hydrogen-bonded assemblies **3a**–**d** were prepared by dissolving the hydrogen bond donor and acceptor in pyridine followed by slow evaporation of the pyridine. The complexes thus formed were dried under vacuum for 24 h prior to characterization. The unsubstituted benzoic acid complex **3a** melts directly from the crystalline to the isotropic phase without the formation of an intervening LC phase. The supramolecular assembly **3b** exhibited a focal-conic texture, characteristic of SmA between 124 and 127°C, while **3c**, where $R = NO_2$, showed SmA and N phases, and **3d** showed a threaded texture, characteristic of a N phase from 135 to 171°C. The phase transitions of these mesogens are summarized in table 3.

Table 3. Phase transition temperatures (°C) of **3a**–**e**: Cr = crystalline, N = nematic, SmA = smectic A and I = isotropic phase.

| Compound | Heating | Cooling |
|---|---|---|
| **3a** | Cr 95 I | |
| **3b** | Cr 124 SmA 127 I | I 126 SmA 112 Cr |
| **3c** | Cr 151 SmA 156 N 170 I | I 168 N 156 SmA 150 Cr |
| **3d** | Cr 135 N 171 I | I 169 N 131 Cr |

These studies suggest that an electron attracting *para*-substituent on the benzoic acid results in stabilization of the LC phase which is in agreement with earlier reports on hydrogen-bonded liquid crystals generated using 4-(4-$n$-hexyloxyphenyl) pyridine and substituted benzoic acid derivatives [12].

### 2.3. *Thermal properties of the binary mixtures*

Studies on the LC properties of stoichiometric complexes **1a**–**e** and **2a**–**e** indicated the formation of unique materials. The phase transition temperatures for these materials are sharp and highly reproducible. Further confirmation for the formation of hydrogen-bonded materials was obtained by studying the thermal properties of binary mixtures of the hydrogen bond donor and acceptor in varying proportions. We investigated the binary phase diagrams for three representative mixtures, namely (a) 4-hexyloxyphenyl-4′-azopyridine (6-PAP)/4-hexyloxybenzoic acid (figure 5); (b) 4-dodecyloxyphenyl-4′-azopyridine (12-PAP)/4-dodecyloxybenzoic acid (figure 6); and (c) 4-pyridylazo-4′-phenyl-$n$-tetradecanoate (PPT)/4-octyloxybenzoic acid (figure 7). The LC properties of the binary mixtures were examined by POM and DSC at a heating/cooling rate of 5°C min$^{-1}$.

The binary mixtures formed between 6-PAP and 4-$n$-hexyloxybenzoic acid mainly exhibited a N phase. In addition a SmA phase was observed in mixtures containing 30–60 mol % of 6-PAP. Some of the key features noticeable in this phase diagram (figure 5) are discussed below. The presence of two eutectic points around 20 and 60 mol % of 6-PAP strongly supports the formation of pure LC material in the 1 : 1 ratio. However, the absence of an azeotropic maximum for the smectic and nematic mixtures suggests that the interactions between the dimerized alkyloxybenzoic acid and the hydrogen-bonded 1 : 1 stoichiometric compound are not particularly

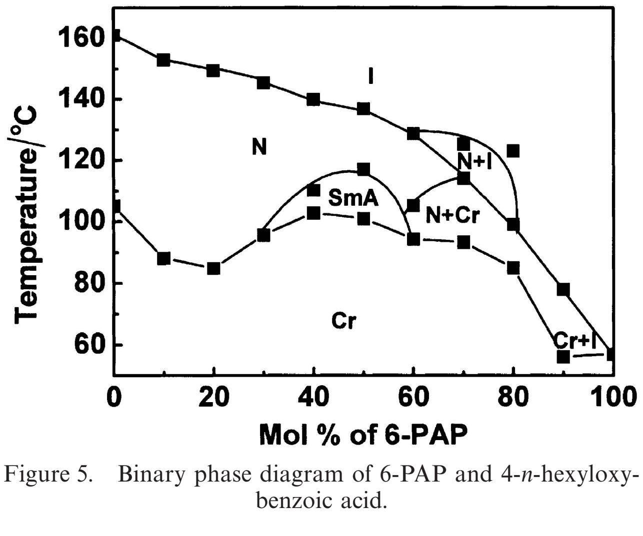


Figure 5. Binary phase diagram of 6-PAP and 4-$n$-hexyloxybenzoic acid.

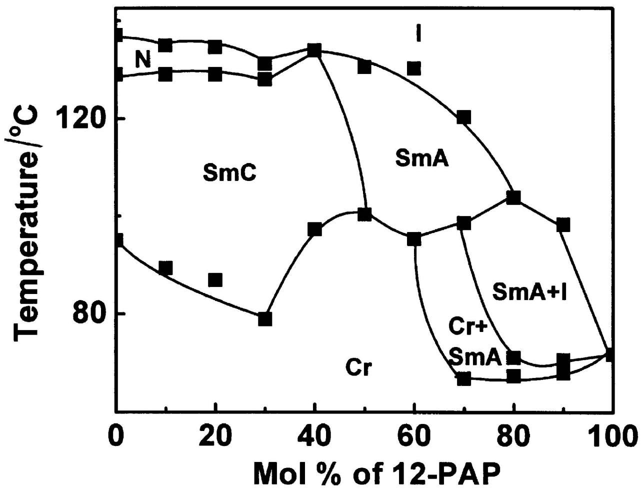


Figure 6. Binary phase diagram of 12-PAP and 4-*n*-dodecyloxybenzoic acid.

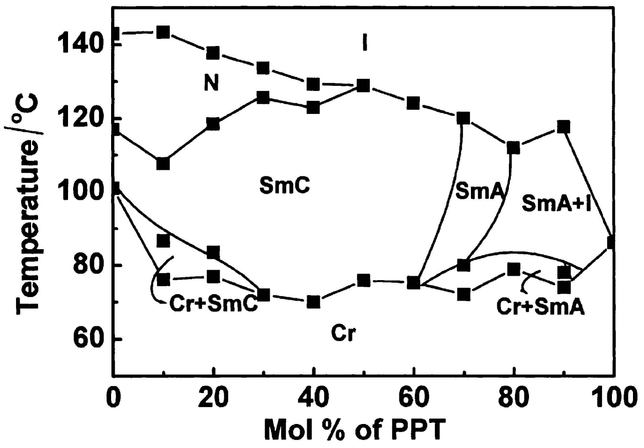


Figure 7. Binary phase diagram of PPT and 4-*n*-octyloxybenzoic acid.

stronger in the nematic phase than in the isotropic liquid state. The SmA–N transition temperature passes through a maximum indicating that, contrary to what happens in the nematic phase, a 1 : 1 stoichiometric mixture does exist in the smectic phase. The presence of a melting maximum for the crystalline mixtures containing 50 mol % of 6-PAP proves without doubt that a well defined material is formed from stoichiometric hydrogen bonding with hexyloxybenzoic acid. Above 60 mol % of 6-PAP biphasic regions between the crystal and the nematic phase as well as the nematic and the isotropic melt were observed by POM and DSC.

Similar observations were made for binary mixtures 12-PAP/4-dodecyloxybenzoic acid (figure 6). The two eutectic points observed for 30 mol % of 12-PAP (at 79°C) and for 70 mol % of 12-PAP (at 67°C) clearly confirmed the formation of pure material on 1 : 1 complexation. Biphasic regions were observed above 60 mol % of 12-PAP between the crystalline and smectic A as well as the smectic A and isotropic phases.

Figure 7 illustrates the phase diagram for the mixture PPT and 4-octyloxybenzoic acid. Extended mesophases were observed in these cases. In addition to a smectic phase, a nematic phase was observed up to 40 mol % of PPT. A smectic C phase was observed below 70 mol % of PPT whereas a SmA phase was observed in the mixtures containing 70–90 mol % of PPT. Figure 7 also illustrates the existence of biphasic regions above and below 50 mol % of PPT

### 2.4. *Isomerization studies*

The *trans-cis*-photoisomerization as well as the thermal *cis-trans*-isomerization of 4-alkoxyphenyl-4′-azopyridines were investigated for a variety of hydrogen-bonding solvents using steady state and time-resolved spectroscopic studies. These results indicate that both hydrogen bonding as well as protonation of the pyridyl moiety bring about a substantial enhancement in the rate of *cis*- to *trans*-isomerization. Hydrogen bonding, as well as protonation of the pyridyl group, will lead to an increase in its electron withdrawing ability resulting in an enhancement in the donor–acceptor nature of the *n*-PAP. Donor/acceptor-substituted azobenzene derivatives have been reported to undergo fast *cis*- to *trans*-thermal isomerization reactions [34, 35].

Photoisomerization studies of these hydrogen-bonded assemblies were also carried out for their liquid crystalline phases. However, associated changes in the phase transition behaviour of these assemblies could not be observed on photolysis of the material in its liquid crystalline phase. The probable reason for this is that at the high temperatures required to obtain the LC phases for these materials, the thermal *cis*- to *trans*-isomerization is very rapid.

## 3. Experimental

### 3.1. *Characterization*

Phase transitions were observed using a Nikon HFX 35A Optiphot polarizing optical microscope equipped with a Linkam THMS 600 heating and freezing stage connected to a Linkam TP92 temperature programmer with a heating/cooling rate of 5°C min$^{-1}$. DSC scans were performed using a du Pont DSC 2010 differential scanning calorimeter attached to a Thermal Analyst 2100 data station under air. IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrophotometer. The electronic spectra were recorded on a Shimadzu Model UV-3101 PC-UV-Vis-NIR scanning spectrophotometer. The $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker DPX 300 MHz FTNMR spectrometer using tetramethylsilane (TMS) as internal standard. Steady state photolyses were carried out on an Oriel optical bench using a 200 W high pressure mercury lamp. Monochromatic light obtained using a 320 nm (for PPT) or 360 nm (in the case of *n*-PAP) band-pass filter was used for photolysis experiments.

### 3.2. *Materials*

Reagent grade reactants and solvents were used as received from suppliers. Extremely dry solvents were prepared by standard procedures. Spectroscopic grade solvents were used for all measurements.

### 3.3. *General procedure for the preparation of 4-n-alkyloxyphenyl-4′-azopyridines (n-PAP)*

4-Hydroxyphenyl-4′-azopyridine (HPAP), *n*-alkyl bromide and sodium hydroxide were dissolved in *N*,*N*-dimethylformamide and the reaction mixture was heated at 100°C for 24 h. It was then cooled to room temperature, added to water and extracted with benzene. The solvent was evaporated and the residue purified by column chromatography using benzene as eluent. The product was recrystallized from ethyl acetate/petroleum ether (1/19), to give a pure sample.

*4-PAP*: m.p. 82°C (yield 60%). IR $\nu_{max}$ (KBr): 2963, 2934, 1598, 1463, 1402, 1311, 1266, 1140, 1068, 973, 830 cm$^{-1}$. UV $\lambda_{max}$ (toluene): 360 nm ($\varepsilon = 20\,287$ M$^{-1}$ cm$^{-1}$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.9 (3H, t, CH$_3$), 1.4–1.5 (2H, m, OCH$_2$–CH$_2$–CH$_2$), 1.7–1.8 (2H, m, OCH$_2$–CH$_2$), 4.0 (2H, t, OCH$_2$), 7.0 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.0 (2H, d, aromatic), 8.8 (2H, d, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 13.79, 19.18, 31.14, 68.16, 114.84, 116.14, 125.57, 146.65 151.15, 157.72, 163.46. Anal: calc for $C_{15}H_{17}ON_3$, C 70.56, H 6.71, N 16.45; found C 70.61, H 7.09, N 16.03%.

*6-PAP*: m.p. 57°C (yield 62%). IR $\nu_{max}$ (KBr): 2935, 2868, 1604, 1467, 1404, 1312, 1259, 1140, 1025, 841 cm$^{-1}$. UV $\lambda_{max}$ (toluene): 360 nm ($\varepsilon = 21\,620$ M$^{-1}$ cm$^{-1}$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.9 (3H, t, CH$_3$), 1.4–1.5 (6H, m, OCH$_2$–CH$_2$–CH$_2$), 1.7–1.8 (2H, m, OCH$_2$–CH$_2$), 4.0 (2H, t, OCH$_2$), 7.0 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.0 (2H, d, aromatic), 8.8 (2H, d, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.01, 22.57, 25.65, 29.68, 31.53, 68.50, 114.86, 116.14, 125.58, 146.68, 151.20, 157.46, 162.90. Anal: calc for $C_{17}H_{21}ON_3$, C 72.05, H 7.46, N 14.82; found C 71.59, H 7.79, N 14.83%.

*8-PAP*: m.p. 67°C (yield 66%). IR $\nu_{max}$ (KBr): 2932, 2864, 1599, 1471, 1414, 1320, 1261, 1137, 1017, 843 cm$^{-1}$. UV $\lambda_{max}$ (toluene): 360 nm ($\varepsilon = 19\,258$ M$^{-1}$ cm$^{-1}$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.9 (3H, t, CH$_3$), 1.4–1.5 (10H, m, OCH$_2$–CH$_2$–CH$_2$), 1.7–1.9 (2H, m, OCH$_2$–CH$_2$), 4.0 (2H, t, OCH$_2$), 7.0 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.0 (2H, d, aromatic), 8.8 (2H, d, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.15, 22.70, 26.04, 29.17, 29.27, 29.37, 31.84, 68.56, 114.92, 116.21, 125.64, 146.85, 151.23, 156.96, 162.79. Anal: calc for $C_{19}H_{25}ON_3$, C 73.28, H 8.09, N 13.49; found C 73.12, H 8.08, N 13.55%.

*10-PAP*: m.p. 63°C (yield 64%). IR $\nu_{max}$ (KBr): 2929, 2862, 1598, 1507, 1420, 1413, 1253, 1139, 1014, 841 cm$^{-1}$. UV $\lambda_{max}$ (toluene): 360 nm ($\varepsilon = 20\,600$ M$^{-1}$ cm$^{-1}$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.9 (3H, t, CH$_3$), 1.3–1.5 (14H, m, OCH$_2$–CH$_2$–CH$_2$), 1.7–1.9 (2H, m, OCH$_2$–CH$_2$), 4.0 (2H, t, OCH$_2$), 7.0 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.0 (2H, d, aromatic), 8.8 (2H, d, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.63, 23.18, 26.51, 29.64, 29.72, 29.85, 30.08, 30.13, 32.41, 68.89, 115.29, 116.66, 126.10, 147.18, 151.55, 157.45, 163.30. Anal: calc for $C_{21}H_{29}ON_3$, C 74.29, H 8.61, N 12.38%. found C 73.76, H 9.04, N 12.36%.

*12-PAP*: m.p. 71°C (yield 60%). IR $\nu_{max}$ (KBr): 2927, 2856, 1597, 1497, 1468, 1409, 1313, 1253, 1139, 1006, 921, 844 cm$^{-1}$. UV $\lambda_{max}$ (toluene): 360 nm ($\varepsilon = 21\,454$ M$^{-1}$ cm$^{-1}$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.9 (3H, t, CH$_3$), 1.3–1.5 (18H, m, OCH$_2$–CH$_2$–CH$_2$), 1.7–1.9 (2H, m, OCH$_2$–CH$_2$), 4.0 (2H, t, OCH$_2$), 7.0 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.0 (2H, d, aromatic), 8.8 (2H, d, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.56, 23.23, 26.51, 29.64, 29.70, 29.85, 29.95, 30.08, 30.15 30.23, 32.41, 68.89, 115.29, 116.66, 126.10, 147.17, 151.55, 157.89, 163.35. Anal: calc for $C_{23}H_{33}ON_3$, C 75.16, H 9.05, N 11.43; found C 74.88, H 10.45, N 11.77.

### 3.4. *4-Pyridylazo-4′-phenyl-n-tetradecanoate (PPT)*

A mixture of 4-hydroxyphenyl-4′-azopyridine (HPAP) and triethylamine was dissolved in dichloromethane. To this reaction mixture *n*-tetradecanoic acid chloride was added dropwise. After heating at 40°C for 36 h, the reaction mixture was cooled to room temperature, added to cold water and shaken with dichloromethane. The organic layer was washed with sodium hydroxide (10%, aqueous). The solvent was evaporated off and the crude product purified by column chromatography using ethyl acetate/petroleum ether (1/19) as eluent to give a pure sample; m.p. 86°C (72%). IR $\nu_{max}$ (KBr): 2924, 2858, 1755, 1587, 1487, 1409, 1220, 1150, 925, 848 cm$^{-1}$. UV $\lambda_{max}$ (toluene): 323 nm ($\varepsilon = 16\,353$ M$^{-1}$ cm$^{-1}$). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.9 (3H, t, CH$_3$), 1.2–1.4 (20H, m, CH$_2$–CH$_2$–CH$_2$–CO), 1.7–1.8 (2H, m, CH$_2$–CH$_2$–CO) 2.5–2.6 (2H, t, CH$_2$–CO), 7.3–7.5 (2H, d, aromatic), 7.7 (2H, d, aromatic), 8.0 (2H, d, aromatic), 8.8 (2H, d, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.10, 22.67, 24.83, 29.07, 29.22, 29.33, 29.42, 29.57, 29.62, 29.66, 31.90, 34.41, 116.88, 122.56, 124.97, 149.82, 154.32, 157.97, 171.77. Anal: calc for $C_{25}H_{35}O_2N_3$, C 73.31, H 8.61, N 10.25; found C 72.82, H 9.59, N 10.95%.

### 3.5. *Preparation of the hydrogen-bonded assemblies*

Equimolar quantities of the hydrogen bond acceptor and the corresponding 4-*n*-alkyloxybenzoic acid were thoroughly mixed, heated above the melting points and slowly cooled. The material obtained after cooling, in each case, was used for studying the phase transition behaviour.

Binary mixtures of hydrogen bond donors and hydrogen bond acceptors were prepared by mechanical stirring of the components in the required ratios above their melting temperatures followed by slow cooling.

## 4. Conclusions

Hydrogen-bonded mesomorphic materials were prepared from substituted phenylazopyridines as hydrogen bond acceptors (*n*-PAP and PPT) and 4-*n*-alkyloxybenzoic acids as hydrogen bond donors. These supramolecular materials (**1a**–**e** and **2a**–**e**) exhibit LC properties over a range of temperatures. The binary phase diagrams between the hydrogen bond acceptors and the hydrogen bond donors showed a maximum isotropization temperature for the 50 mol % composition in all cases. This can be attributed to the formation of a 1 : 1 supramolecular assembly by intermolecular hydrogen bonding. Isomerization studies of the azo chromophore present in the phenylazopyridine moiety in different hydrogen bonding solvents showed that the rate of thermal *cis-trans*-isomerization increased with increasing hydrogen bonding ability of the solvents. These hydrogen bonded supramolecular assemblies showed no change in phase transition behaviour on irradiation in the liquid crystalline state; this is probably due to fast recovery of the *trans*-form at the high temperatures required for these materials to show their LC properties.

Financial support from the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India is acknowledged. This is contribution No. RRLT-PRU-154 from the Regional Research Laboratory, Trivandrum.

## References

[1] Kato, T., and Frechet, J. M. J., 1989, *Macromolecules*, **22,** 3818.

[2] Kato, T., and Frechet, J. M. J., 1989, *J. Am. chem. Soc.*, **111,** 8533.

[3] Kumar, U., Frechet, J. M. J., Kato, T., Ujiie, S., and Timura, K., 1992, *Angew. Chem. int. Ed. Engl.*, **31,** 1531.

[4] Kumar, U., and Frechet, J. M. J., 1992, *Adv. Mater.*, **4,** 665.

[5] Bladdon, P., and Griffin, A. C., 1993, *Macromolecules*, **26,** 6604.

[6] Yu, L. J., 1993, *Liq. Cryst.*, **14,** 1303.

[7] Alexander, C., Jariwala, C. P., Lee, C.-M., and Griffin, A. C., 1993, *Polym. Prepr.*, **34,** 168.

[8] Kresse, H., Szulzewsky, I., Diele, S., and Paschke, R., 1994, *Mol. Cryst. liq. Cryst.*, **238,** 13.

[9] Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem. int. Ed. Engl.*, **34,** 1696.

[10] Pourcain, C. B. S., and Griffin, A. C., 1995, *Macromolecules*, **28,** 4116.

[11] Schellhorn, M., and Lattermann, G., 1995, *Macromol. Chem. Phys.*, **196,** 211.

[12] Bernhardt, H., Weissflog, W., and Kresse, H., 1996, *Angew. Chem. int. Ed. Engl.*, **35,** 874.

[13] Koh, K. N., Araki, K., Komori, T., and Shinkai, S., 1995, *Tetrahedron Lett.*, **36,** 5191.

[14] Kato, T., Hirota, N., Fujishima, A., and Frechet, J. M. J., 1996, *J. polym. Sci. A. polym. Chem.*, **34,** 57.

[15] Kato, T., Kihara, H., Ujiie, S., Uryu, T., and Frechet, J. M. J., 1996, *Macromolecules.*, **29,** 8734.

[16] Price, D. J., Adams, H., and Bruce, D. W., 1996, *Mol. Cryst. liq. Cryst.*, **289,** 127.

[17] Kihara, H., Kato, T., Uryu, Y., Ujiie, S., Kumar, U., Frechet, J. M. J., Bruce, D. W., and Price, D. J., 1996, *Liq. Cryst.*, **21,** 25.

[18] Kleppinger, R., Lillya, C. P., and Yang, C., 1997, *J. Am. chem. Soc.*, **119,** 4097.

[19] Goldman, D., Dietel, R., Janietz, D., Schmidt, C., and Wendorff, J. H., 1998, *Liq. Cryst.*, **24,** 413.

[20] Yu, L. J., and Pan, J. S., 1993, *Liq. Cryst.*, **14,** 829.

[21] Paleos, C. M., and Tsiourvas, D., 2001, *Liq. Cryst.*, **28,** 1127.

[22] Mallia, V. A., Antharjanam, P. K. S., and Das, S., 2001, *Chem. Lett.*, 752.

[23] Mallia, V. A., and Das, S., 2001, *Liq. Cryst.*, **28,** 259.

[24] Mallia, V. A., George, M., and Das, S., 1999, *Chem. Mater.*, **11**, 207.

[25] Ikeda, T., and Tsutsumi, O., 1995, *Science.*, **268,** 1873.

[26] Ikeda, T., and Kanazawa, A., 2001, *Molecular Switches*, edited by B. L. Feringa (Weinheim: Wiley-VCH), pp. 362–397.

[27] Ichimura, K., 2000, *Chem. Rev.*, **100,** 1847.

[28] Johnson, S. L., and Rumon, K. A., 1965, *J. phys. Chem.*, **69,** 74.

[29] Odinokov, S. E., Mashkovsky, A. A., Glazunov, V. P., Iogansen, A. V., and Rassadin, B. V., 1976, *Spectrochem. Acta.*, **32A,** 1355.

[30] Demus, D., and Richter, L. 1978, *Textures of Liquid Crystals* (Weinheim: Verlag Chemie).

[31] Kelker, H., and Hatz, R., 1980, *Hand Book of Liquid Crystals* (Weinheim: Verlag Chemie).

[32] Kato, T., Frechet, J. M. J., Wilson, P. G., Saito, T., Uryu, T., Fujishima, A., Jin, C., and Kaneuchi, F., 1993, *Chem. Mater.*, **5,** 1094.

[33] Kang, Y.-S., Kim, H., and Zin, W.-C., 2001, *Liq. Cryst.*, **28,** 709.

[34] Asano, T., and Okada, T., 1984, *J. org. Chem.*, **49**, 4387.

[35] Wildes, P. D., Pacifici, J. G., Irick, G. Jr., and Whitten, D. G., 1971, *J. Am. Chem. Soc.*, **93**, 2004.