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Synthesis and studies of some cholest-5-en-3-ol-(3β)[4-phenylpyridylazo]carbonate-containing supramolecular hydrogen-bonded mesogens

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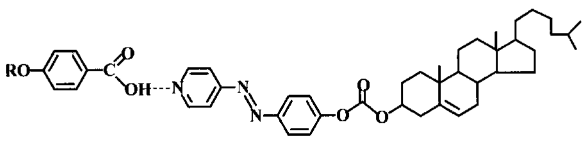
Mesogenic materials containing cholest-5-en-3-ol-(3β)[4-phenylpyridylazo]carbonate (CPPC) and 4-*n*-alkyloxybenzoic acids have been synthesized using hydrogen bonding as a mechanism for self-assembly. Phase diagrams of the binary mixtures of the hydrogen bond donor and acceptor were established using polarizing optical microscopy. The maximum isotropization point was observed for the 50 mol% composition confirming the formation of stable 1:1 complexes due to intermolecular hydrogen bonding. All the supramolecular assemblies built from 1:1 molar ratios of the hydrogen bond donor and acceptor moieties exhibit well defined smectic A (SmA) liquid crystal phases on heating and cooling cycles. The SmA phases exhibited by the complexes are not observed for the individual components. The azobenzene moiety of CPPC undergoes *trans-cis*-photoisomerization with a quantum yield of 0.1 and the activation energy for the thermal *cis-trans*-isomerization was estimated as 92 kJ mol^{-1}.

1. Introduction

Non-covalent interaction between different molecular species has been advantageously used for the design of new supramolecular materials [1, 2]. These materials have been generated through molecular interactions involving hydrogen bonds and ionic bonds, as well as through charge transfer and ion dipolar interactions [3–12]. In recent years hydrogen bonding has been extensively used to generate new monomeric and polymeric liquid crystals wherein the mesomorphism results from the appropriate combination of the hydrogen bond donors and acceptors. Many of the reported studies have utilized the strong hydrogen bonding between pyridyl groups and carboxylic acids for the generation of such liquid crystalline materials.

Cholesterol-containing liquid crystals have attracted considerable attention due to the chiral nature of the molecule which can give rise to cholesteric liquid crystals either in the pure form or when doped into nematic liquid crystals. The characteristic helical structure of cholesteric liquid crystals imparts unique optical properties such as selective reflection of light, thermochromism and, circular dichroism, and these properties have been used to generate coloured glassy materials [13–16]. Studies have shown that systems having linked azobenzene and cholesterol moieties can exhibit marked changes in pitch and wavelength of selective reflection on irradiation [15, 16]. There are however relatively few reports in the area of cholesterol linked supramolecular mesogens [17–20] and to our knowledge no azobenzene-cholesterol linked systems have been prepared in this way. The aim of this study has been to synthesize supramolecular mesogens with cholest-5-en-3-ol-(3β)[4-phenylpyridylazo]carbonate (CPPC) as hydrogen bond acceptor and different 4-*n*-alkyloxybenzoic acids as hydrogen bond donors (see the scheme) and to study their liquid crystalline properties and photoisomerization. The presence of the azo-moiety can impart photoswitching properties to these materials, since irradiation can lead



1 a-e

1a, R = C_4H_9
1b, R = C_6H_{13}
1c, R = C_8H_{17}
1d, R = $C_{10}H_{21}$
1e, R = $C_{12}H_{25}$

Scheme.

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to photoisomerization of the azo moiety from the *trans*- to the *cis*-form. Earlier studies on azobenzene-derived liquid crystals as well as on liquid crystals doped with azobenzene have shown that the *cis*-form tends to destabilize the liquid crystalline phase [21–24]. Sequential UV and visible light irradiation of supramolecular hydrogen-bonded liquid crystalline polymers containing azobenzene units has also been reported to bring about reversible nematic to isotropic phase transitions [24].

2. Results and discussion

2.1. *Synthesis*

The hydrogen-bonded supramolecular mesogens used in the present study were prepared as follows. CPPC was synthesized by heating cholesteryl chloroformate and 4-hydroxyphenylazopyridine at reflux in a mixture (1 : 1) of methanol and chloroform. All compounds were characterized on the basis of spectral data. The hydrogen-bonded complexes were synthesized by thoroughly mixing equimolar quantities of CPPC with 4-*n*-alkyloxybenzoic acids and heating above the melting points of the mixtures for a few minutes. The mixture was then allowed to cool slowly to yield the liquid crystalline materials **1a–e** (see the scheme).

2.2. *Thermal properties*

The pyridyl group strongly hydrogen bonds with carboxylic acids, and the supramolecular materials formed via hydrogen bonding between CPPC and 4-*n*-alkyloxybenzoic acids showed interesting liquid crystalline properties. The thermal behaviour of the complexes confirms the selective formation of the hydrogen-bonded mesogens shown in the scheme. All the complexes behave as single liquid crystalline materials and show clear phase transitions. The thermal properties of the complexes are different from those of the individual components. The phase transitions of these compounds were studied by hot stage polarizing optical microscopy (POM) and X-ray diffraction (XRD). POM of **1a** ($n = 4$) showed a focal-conic texture characteristic of a SmA phase [25] from 175.6 to 185.6°C in the heating cycle and from 185.5 to 154.2°C in the cooling cycle. The phase transition temperatures were reproducible over several heating and cooling cycles. The supramolecular assembly **1b** ($n = 6$) exhibits a SmA phase from 109.9 to 158.4°C in the heating cycle and from 157.2 to 91.2°C in the cooling cycle. **1c** undergoes a crystal to SmA transition at 108°C and isotropizes at 155°C. Complexes **1d** and **1e** show SmA focal-conic textures from 108.7 to 143.6°C and from 130 to 162°C, respectively. The dependence of the phase transition temperatures of the complexes on chain length of the alkyl group is shown in figure 1 and the phase transition temperatures of these assemblies are summarized in table 1. The observed dependence of the transition points on alkyl chain length is similar to that reported for well known smectics [26]. A similar dependence was also reported for the smectic liquid crystals generated via hydrogen bonding between bipyridyl and alkyloxybenzoic acids [7]. The SmA phase of compound **1c** was also confirmed by XRD: the diffraction pattern of **1c** at 140°C showed a sharp ring at 36.7 Å associated with the molecular smectic layers. The length of the supramolecular assembly **1c** in its all *trans*-conformation is 37.5 Å (calculated using PC-Spartan software obtained from Wavefunction, Inc.; 18401 program). The slightly smaller observed layer spacing may be attributed to folding of the alkyl chain from its all-*trans*-conformation. The diffraction pattern also shows a diffuse ring at 5.6 Å due to the lateral liquid-like correlation of the molecules within the layers. The layer spacings were the same at 150°C.

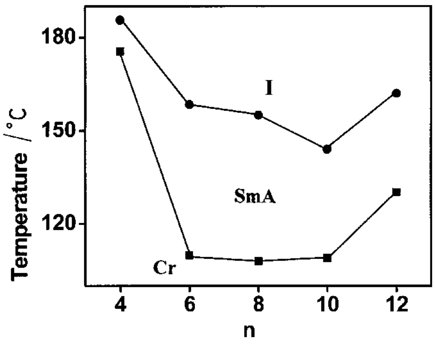

Figure 1. Plot of transition temperature against the number of carbon atoms (n) in the alkyl chain for the 1 : 1 hydrogen bonded complexes, **1a**–**e**.

Table 1. Phase transition temperatures of hydrogen bonded assemblies.

	Phase transition temperature/°C	
Compound	Heating	Cooling
1a	Cr 175.6 SmA 185.6 I	I 185.5 SmA 154.2 Cr
1b	Cr 109.9 SmA 158.4 I	I 157.2 SmA 91.2 Cr
1c	Cr 108 SmA 155 I	I 155 SmA 108 Cr
1d	Cr 109 SmA 144 I	I 140 SmA 70 Cr
1e	Cr 130 SmA 162 I	I 155 SmA 120 Cr

The O–H bands around 2581 and 1950 cm^{-1} observed for the complexes in the IR spectra are indicative of hydrogen bonding [7, 27, 28], these bands replacing the O–H band around 3000 cm^{-1} observed for the hydrogen bonded dimers in the pure acid [26, 27]. The absence of the 3000 cm^{-1} band is clearly indicative of the formation of the 1 : 1 hydrogen-bonded 50% mixtures. For compounds mixed in ratios other than 1 : 1, such as the mixture containing 30 mol % of CPPC, both the O–H bands around 2500 and 1920 cm^{-1} as well as those around 3000 cm^{-1} were observable, indicating the coexistence of the hydrogen-bonded assemblies with hydrogen-bonded dimers.

2.3. *Thermal properties of the binary mixtures*

The liquid crystalline properties of the binary mixtures were examined by POM using a heating/cooling rate of 5°C min^{-1}. 4-*n*-Dodecyloxybenzoic acid shows a smectic C (SmC) liquid crystalline phase from 95 to 129°C and a nematic phase from 129 to 137°C; the compound CPPC melts sharply at 198°C. Figure 2 shows the binary phase diagram for mixtures of CPPC and 4-*n*-dodecyloxybenzoic acid; the binary mixture containing 10 mol % of CPPC does not show a nematic phase. The mixture showed a broken fan texture and a fine four-brush schlieren texture, which clearly indicates the presence of SmC from 92 to 134°C. The 20 mol % CPPC mixture also showed a SmC phase from 88.2 to 144.3°C. The lowest melting composition was the binary mixture of 30 mol % CPPC and the acid. This mixture melts to a SmA phase at 84.4°C, confirmed by its focal-conic texture, and isotropizes at 152.8°C. The maximum temperature range of the liquid crystalline phase was observed at this concentration. Mixtures of 40 and 60 mol % of hydrogen bond acceptor and acid exhibit smectic A phases from 127.3 to 155.3°C and 117.8 to 154.2°C, respectively. The 70, 80 and 90 mol % compositions of CPPC do not show any liquid crystalline phase in the heating and cooling cycles. The melting points for these compositions were 150.8, 153.6 and 183.7°C, respectively.

The 50 mol % mixture exhibits a well defined SmA phase from 130°C until isotropization at 162°C, which confirms the formation of a stable supramolecular assembly. It is important to note that in all binary mixtures other than 50 mol %, the liquid crystalline phase coexists with a crystalline phase or an isotropic melt. Additional evidence for the formation of a pure liquid crystalline material by supramolecular hydrogen bonding in the 50% mixture is provided by the existence of the two eutectic points obtained for the 30 and 60 mol % mixtures (figure 2).

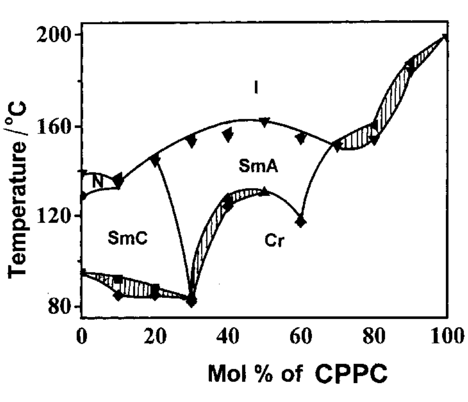

Figure 2. Binary phase diagram of CPPC and 4-*n*-dodecyloxybenzoic acid. Shaded portions denote regions showing two coexisting phases.

2.4. *Isomerization studies*

The photoisomerization of CPPC dissolved in toluene was examined by steady state photolysis experiments using a 200 W high pressure mercury lamp equipped with a 320 nm band pass filter as the light source. The quantum yield of photoisomerization ($\Phi_{trans\text{-}cis}$) determined using azobenzene as actinometer [29] was found to be 0.13 in toluene. The rate of thermal *cis*- to *trans*-isomerization following irradiation was determined spectrophotometrically by monitoring the increase in absorbance at the π-π^* maxima of the *trans*-isomer (320 nm), which is accompanied by a decrease in the absorbance at 450 nm. The *cis-trans*-isomerization which occurs in the dark follows first order kinetics and the rate constant for the process was 2.9×10^{-5} s^{-1} at 25°C. Based on the dependence of the rate constants for the thermal isomerization on temperature, the activation energy of this process, calculated using the Arrhenius equation was 92 kJ mol^{-1}.

In toluene CPPC has an absorption maximum at 323 nm. In solvents of the alcohol type, the absorption maximum undergoes a progressive hypsochromic shift with increasing hydrogen bond donating strength of the alcohol (table 2). However when acetic acid was added to the solution of CPPC in toluene, a progressive bathochromic shift was observed (table 2). In order to examine whether this shift could arise due to protonation of the azopyridyl moiety of CPPC, we also studied the effect of adding hydrochloric acid (> 10 μM) to a methanolic solution of CPPC. In the presence of hydrochloric acid the protonated species of CPPC would be formed and this has an absorption maximum centred around 343 nm.

The *cis-trans*-isomerization of CPPC in alcoholic solvents was studied using steady state photolysis; the rate constants for the processes are shown in table 2. It

Table 2. Absorption maxima and rate constants for the *cis-trans*-isomerization of CPPC in different solvents.

Solvent	λ_{max}/nm	Rate constant/s^{-1} (at 25°C)
Toluene	323	2.9×10^{-5}
Methanol	319	6.2×10^{-4}
Ethanol	318	2.0×10^{-3}
Trifluoroethanol	314	7.4×10^{-2}
Toluene : acetic acid (3 : 2)	325	7.2
Acetic acid	330	66.8
Hydrochloric acid in methanol (10 μM)	343	103.7

becomes evident that the rate of *cis-trans*-isomerization increases with hydrogen bond donating strength of the solvent.

In the presence of acetic acid, however, no change could be observed in the absorption spectrum of CPPC on steady state irradiation. This is attributed to rapid thermal *cis*- to *trans*-isomerization. To investigate this, we studied the isomerization of CPPC in such solvents using the nanosecond laser flash photolysis technique. The details of the experimental set-up have been described previously [30]. The third harmonic (355 nm) of a Nd:Yag pulsed laser (pulse duration 10 ns, energy 60 mJ/pulse) was used to excite CPPC and the optical changes were monitored at 330 nm using a laser spectrometer (Applied Photophysics model LKS-20). A 320 nm band pass filter was placed between the sample and the analyser lamp to prevent secondary photolysis of the *cis*-isomer formed in the photoisomerization. Figure 3 shows the absorption–time profile at 330 nm, following the laser pulse excitation of a solution of CPPC in acetic acid. Following the laser pulse, bleaching is observed due to conversion of the *trans*-CPPC to its *cis*-form. The reversal of the bleaching corresponds to the thermal *cis-trans*-isomerization. The rate constants for this process measured for solutions of CPPC in acetic acid and toluene:acetic acid (3:2) (table 2) are two to three orders of magnitude higher than those observed for the alcoholic solvents. The rate of isomerization increases with the concentration of acetic acid. In methanolic solutions of CPPC containing hydrochloric acid (10 μM) the rate constant of isomerization was greater (table 2).

These results indicate that both hydrogen bonding and protonation result in enhancement in the rate of *cis-trans*-isomerization of CPPC. The pK_a of acetic acid (4.72) and alkoxybenzoic acids (~4.5) are similar. The absorption spectral shifts of CPPC in solutions containing acetic acid are suggestive of partial protonation of the pyridyl moiety. However for the 1:1 ratio of CPPC and acid, hydrogen bonding in the assemblies is expected to be the predominant interaction. Regardless of the exact nature of this interaction, the rate of thermal isomerization in the assemblies is expected to be much higher than for the parent compound.

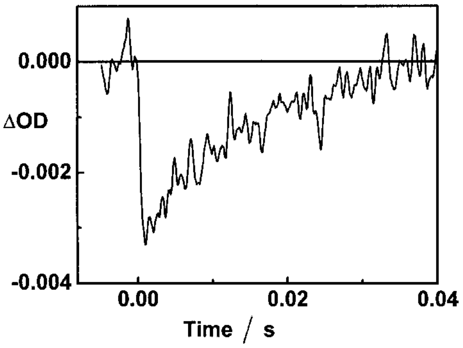

Figure 3. Transient absorption–time profile recorded at 330 nm, following 355 nm laser pulse excitation of CPPC in acetic acid.

The effect of photoirradiation of **1c** was studied at 120°C. A thin film of the assembly was prepared by heating it to the isotropic state and slowly cooling to 120°C. At this temperature **1c** exists in the smectic A (SmA) state. On photoirradiation, isomerization should result in the formation of the *cis*-form of the azobenzene moiety. Earlier studies have shown that build up of the *cis*-form of azobenzene derivatives can lead to destabilization of the liquid crystalline phase [21–24]. In the present study, photoirradiation did not result in any observable change in the phase transition behaviour of **1c**. This may be attributed to the rapid thermal conversion back of the *cis*- to the *trans*-form, which could occur very rapidly at 120°C.

3. Experimental

3.1. *Characterization*

Phase transitions were observed using a Nikon HFX 35A Optiphot polarized light microscope, equipped with a Linkam THMS 600 heating and cooling stage connected to a Linkam TP92 temperature programmer. XRD studies were carried out using CuK_α ($\lambda = 1.54$ Å) radiation from a rotating anode X-ray generator (Rigaku) and the diffraction pattern was collected on an image plate detector (Marresearch). IR spectra were recorded on a Perkin Elmer Model 882 infrared spectrophotometer. The electronic spectra were recorded on a Schimadzu 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 (intensity $= 9.3 \times 10^{-8}$ Einstein min^{-1}) obtained by using a 320 nm band pass filter was used for the irradiation experiments.

3.2. *Materials*

Reagent grade reagents 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. *4-n-Alkyloxybenzoic acids*

These were prepared from 4-hydroxybenzoic acid by a reported procedure [31] and characterized by spectral analyses and measurement of phase transition temperatures. These acids exhibited the following phases.

a, $n = 4$, Cr 147 N 160 I; **b**, $n = 6$, Cr 105 N 153 I; **c**, $n = 8$, Cr 101 SmC 117 N 143 I; **d**, $n = 10$, Cr 97 SmC 122 N 142 I; **e**, $n = 12$, Cr 95 SmC 129 N 137 I (°C).

3.4. *4-Hydroxyphenylazopyridine*

This compound was prepared by diazotization of 4-aminopyridine and coupling with phenol following a reported procedure [32]; the product was recrystallized from ethyl acetate.

3.5. *Cholest-5-en-3-ol-(3β)[4-phenylpyridylazo]carbonate (CPPC)*

To a solution of 4-hydroxyphenylazopyridine (200 mg, 1 mmol) in methanol (10 ml), pyridine (100 mg) was added and the mixture heated at reflux for 30 min. To this, a solution of cholesteryl chloroformate (450 mg, 1 mmol) in chloroform was added dropwise. The reaction mixture was heated at reflux for an additional period of 6 h, following which the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (100–200 mesh) using chloroform as eluent to give 175 mg (30%) of the compound CPPC, m.p. 197–198°C. UV λ_{max} (toluene) 323 nm (ε 14494 M^{-1} cm^{-1}). IR (KBr) ν_{max} 2939, 2366, 1766, 1543, 1377, 1251, 1222, 852 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 0.6–2.5 (44H, m, cholesteric), 4.6 (1H, m, OCH), 5.43 (1H, m, vinylic), 6.7–6.9 (2H, d, aromatic), 7.2–7.5 (2H, d, aromatic), 7.8–8.1 (4H, d, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.81, 18.67, 19.18, 21.00, 22.52, 22.76, 23.83, 24.22, 27.65, 27.92, 28.16, 31.80, 35.74, 36.16, 36.48, 36.78, 37.89, 39.47, 39.68, 40.15, 42.24, 49.94, 56.15, 56.59, 78.59, 121.31, 124.95, 139.36, 151.74, 152.36, 152.57.

3.6. *Preparation of the hydrogen bonded assemblies* [11]

Equimolar quantities of CPPC and the corresponding 4-*n*-alkyloxybenzoic acids were thoroughly mixed and heated above the melting points and slowly cooled. The material obtained after cooling was used in each case for studies of the phase transition behaviour.

Binary mixtures of CPPC and 4-*n*-dodecyloxybenxoic acid were prepared by mechanical stirring of the components in the required ratios above their melting temperatures followed by slow cooling [12].

4. Conclusions

Supramolecular hydrogen-bonded assemblies containing cholesterol and azobenzene linked moieties were prepared from CPPC and 4-*n*-alkyloxybenzoic acids ($n = 4$, 6, 8, 10 and 12). All assemblies showed a SmA liquid crystalline phase over a range of temperatures. In this series, the maximum range of SmA phase was shown by **1b** ($n = 6$). The binary phase diagram between the hydrogen bond acceptor and 4-*n*-dodecyloxybenzoic acid showed a maximum isotropization temperature for the 50 mol % composition; this can be attributed to the formation of a 1:1 supramolecular assembly by intermolecular hydrogen bonding. The temperature range of the liquid crystalline phase is a maximum for the 30 mol % mixture of H-bond donor and acceptor; this exhibits the SmA phase from 84.4 to 152.8°C. The quantum yield of photoisomerization of *trans-cis* ($\Phi_{trans\text{-}cis}$) of CPPC was found to be 0.11 in toluene; the activation energy for the thermal *cis-trans*-isomerization was 90 kJ mol^{-1}. The absence of any photoinduced phase change on irradiation of the SmA phase of **1c** is attributed to rapid thermal conversion of the *cis*- back to the *trans*-form at the temperature required for the formation of the smectic phase. The enhancement in the rates of *cis-trans*-isomerization in the hydrogen-bonded assemblies is also a contributing factor. CPPC can be used as a dopant in non-hydrogen bonding, room temperature liquid crystals for photoswitching applications. Currently we are exploring these aspects, as well as systems wherein the liquid crystalline phase of such photoswitchable hydrogen-bonded assemblies can be observed at lower temperatures.

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