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## Liquid Crystals

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### Properties of thermotropic liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and benzoic acid, 4-chlorobenzoic acid or 4-methylbenzoic acid

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# Properties of thermotropic liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and benzoic acid, 4-chlorobenzoic acid or 4-methylbenzoic acid

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Supramolecular liquid crystalline complexes have been obtained from binary mixtures of 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles with benzoic acid, 4-chlorobenzoic acid or 4-methylbenzoic acid. Neither the oxadiazole derivatives nor the carboxylic acids are mesomorphic, but the H-bonded complexes are. Their liquid crystalline properties were investigated by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction.

## 1. Introduction

The first compounds found to exhibit liquid crystalline behaviour due to hydrogen bond formation were aromatic carboxylic acids [1–5]. These compounds dimerize through intermolecular hydrogen bonds leading to a lengthening of the rigid-rod moiety, which in turn induces liquid crystallinity. However, the role of hydrogen bonding interactions in the formation and/or stabilization of liquid crystalline phases has been recognized only in the last ten years, and a large number of supramolecular liquid crystals obtained through hydrogen bonding interaction of complementary molecules have been extensively studied [6–16].

Mixtures of unlike hydrogen-bonded molecules producing liquid crystals frequently involve donor molecules derived from carboxylic acids and acceptor molecules derived from pyridine, 4,4'-bipyridine or stilbazoles. Previously, we reported the first example of pyridine derivatives containing the thiadiazole ring in their structure [15]. These compounds were used as proton acceptors in the formation of mesomorphic H-bonded complexes with 4-*n*-nonyloxybenzoic acid as proton donor.

Recently, we also reported the first example of angular hydrogen-bonded complexes containing double hydrogen bonds formed by 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles (non-mesogenic) and 2,5-thiophene

dicarboxylic acid (non-mesogenic) [17]. In continuation of the earlier work on hydrogen-bonded complexes of 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles (series **1a–e**), we report here a new series of liquid crystalline complexes involving intermolecular hydrogen bonding between the oxadiazoles and benzoic acid, 4-methylbenzoic acid or 4-chlorobenzoic acid. These hydrogen-bonded complexes contain only a single hydrogen bond in each system and showed different behaviour from the complexes described previously [17]. The former complexes show an enantiotropic nematic phase, whereas the new hydrogen bonded-complexes display an enantiotropic smectic A (SmA) phase. It is interesting to note that both the oxadiazole derivatives (series **1a–e**) and the carboxylic acids are non-mesomorphic alone, therefore the hydrogen bonding is responsible for the formation of liquid crystals in the binary mixtures.

## 2. Experimental

### 2.1. Characterization

Transition temperatures and textures of the mesophases were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage.

Differential scanning calorimetry (DSC) was conducted on a Rheometric DSC-V calorimeter with heating and cooling rates of 5°C min<sup>-1</sup>. The apparatus was calibrated with an indium standard.

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The X-ray diffraction (XRD) patterns were obtained with a pinhole camera (Antoon-Paar) operating with a point-focused Ni-filtered Cu-K $\alpha$  beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated with a variable temperature oven. The patterns were collected on flat photographic films. The capillary axis and the film were perpendicular to the X-ray beam; spacings were obtained via Bragg's law.

## 2.2. Synthesis

The 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles (series **1a–e**) were synthesized and characterized according to our previously reported procedure [17]. The proton donors benzoic acid (99% purity), 4-methylbenzoic acid (99% purity) and 4-chlorobenzoic acid were used as received from Aldrich.

The hydrogen-bonded complexes were prepared by slow evaporation from a chloroform solution containing an equimolar amount of H-bonding donor and H-bonding acceptor moieties, followed by drying *in vacuo* at 60°C. Before evaporation, the solutions were stirred at room temperature for 24 h. Figure 1 shows the structures of the proton acceptors (series **1a–e**) and their H-bonded complexes (series **2**, **3** and **4**) with the corresponding proton donors.

## 3. Results and discussion

### 3.1. Mesomorphic properties

All the H-bonded complexes of series **2a–e** show mesomorphic properties; the complexes behave as a single component and show clear phase transitions and homogeneous mesophases. DSC and polarizing optical microscopy (POM) showed that the homologues with

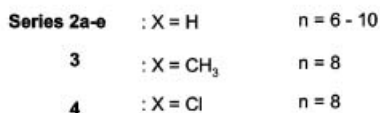
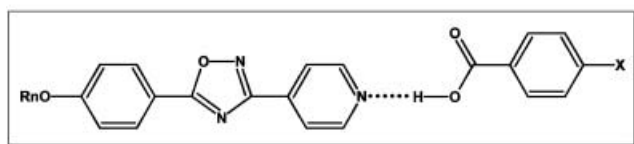
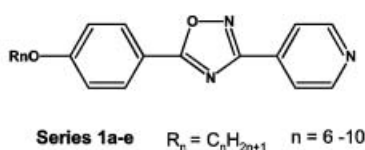


Figure 1. Representation of H-bonded acceptor moieties (series **1a–e**) and H-bonded complexes (series **2a–e**, **3** and **4**).

$n=7–10$  (**2b–2e**) exhibit an enantiotropic smectic A (SmA) mesophase, whereas the homologue with  $n=6$  (**2a**) shows a monotropic transition (see table 1 and figure 2). The optical textures observed upon slow cooling from the isotropic melt clearly showed the existence of an orthogonal SmA phase, which was characterized by its typical focal-conic, polygonal textures and homeotropic alignment.

The 1,2,4-oxadiazole derivatives (series **1a–e**) have a pyridine unit at the end of the rigid core and only one lateral alkoxy chain, and are non-mesomorphic. The H-bonded complexes (series **2a–e**) obtained by interaction of the compounds of the series **1a–e** with benzoic acid display liquid crystalline properties. The intermolecular H-bond leads to a lengthening of the rigid-rod moiety, which in turn induces liquid crystallinity. The H-bonded complexes also have only one lateral alkoxy chain; this is in contrast to conventionally calamitic liquid crystals that require two lateral alkyl chains or two other end groups.

### 3.2. Effect on mesomorphic properties of the benzoic acid substituent

The mesophase stability of a liquid crystalline compound is dependent mainly on the intermolecular interactions, in which molecular polarity, polarizability and electronic factors play an important role [18]. In order to study the effect of substituents on the liquid crystals properties, H-bonded complexes **3** and **4** were prepared between 3-(4-pyridyl)-5-(4-*n*-octyloxy)phenyl-1,2,4-oxadiazole (**1c**) and 4-methylbenzoic acid or 4-chlorobenzoic acid (weak inductor and weak subtractor of electron density), respectively. The H-bonded complexes **2c**, **3** and **4** display an enantiotropic SmA phase. Complex **3** also shows an enantiotropic nematic (N) phase. Complexes **3** and **4** show a higher isotropization temperature and broader mesomorphic range than complex **2c** ( $n=8$ ) (see table 2 and figure 3).

The thermal data presented in table 2 show that the introduction of the methyl group in the 4-position of the benzoic acid (complex **3**) produces the highest mesomorphic range. In this case, lateral interactions are promoted by the methyl group, and the flexibility at the end of the structure, as well as the raised superficial molecular area, favours the London dispersive forces.

With regard to complex **4**, due to repulsive forces the intermolecular distances are bigger, therefore the ease of packing in the mesomorphic state is less. On the other hand, the conjugative effect results in a dipole moment directed opposite to the bond moment of chlorine in the molecule, making packing less effective [18, 19].

Since the proton donor and proton acceptor molecules show no liquid crystalline properties alone, the

Table 1. Transition temperatures and enthalpies for the H-bonded complexes for series **2a–e**: Cr=crystal, SmA=smectic A, I=isotropic.

Series <b>2</b>	<i>n</i>	Transition	Temperature/°C		Enthalpy/J g <sup>-1</sup> by DSC data
			by POM	by DSC	
<b>a</b>	6	Cr–I	112	113.2	77.2
		I–SmA	105	104.8	–1.02
		SmA–Cr	104	103.6	–72.5
<b>b</b>	7	Cr–SmA	96	97.3	77.8
		SmA–I	104	103.4	10.4
		I–SmA	101	102.2	–10.6
		SmA–Cr	97	96.5	–72.6
<b>c</b>	8	Cr–SmA	99	99.7	41.0
		SmA–I	107	106.8	10.6
		I–SmA	104	104.9	–10.8
		SmA–Cr	99	98.8	–40.6
<b>d</b>	9	Cr–SmA	85	86.2	17.8
		SmA–I	103	104.2	6.07
		I–SmA	101	102.6	–5.1
		SmA–Cr	80	79.3	–16.9
<b>e</b>	10	Cr–SmA	87	88.1	30.6
		SmA–I	112	111.3	12.8
		I–SmA	110	110.6	–11.3
		SmA–Cr	83	82.6	–25.9

hydrogen bonding is responsible for formation of the mesophases.

### 3.3. X-ray diffraction studies of the complexes

The nature of the mesophases of complexes **2**, **3** and **4** was confirmed by X-ray diffraction. X-ray patterns were taken at high temperature in the smectic mesophases of the three complexes and also in the nematic mesophase of complex **3**.

In the case of the smectic mesophases, the diffraction patterns are consistent with a smectic A structure. The diffractograms contain a sharp, strong reflection at

small angles that corresponds to the interlayer spacing (layer thickness). The orthogonal character of the smectic structure is confirmed by the fair agreement between the measured layer thickness *d* and the complex length in its fully-extended conformation *L*, estimated from Dreiding stereomodels, see table 3. Therefore, it is concluded that there is no tilt in the layers and the molecular long axis is oriented orthogonal to the smectic plane.

At large angles the patterns exhibit only a diffuse, broad halo that is characteristic of the liquid-like order of the molecules within the layers, and corresponds to a mean distance of about 4.6 Å. This means

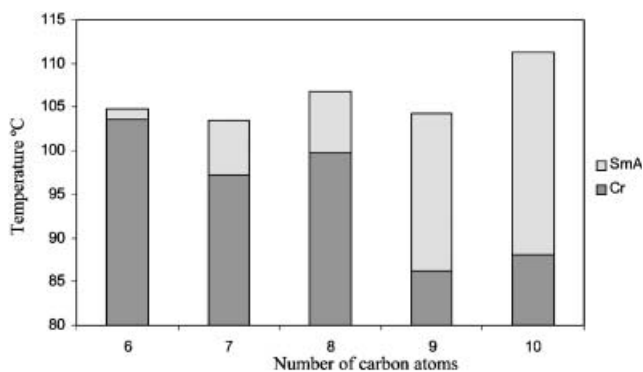


Figure 2. Plot of transition temperature versus the number of carbon atoms in the alkoxy chain for the H-bonded complexes of series **2a–e**.

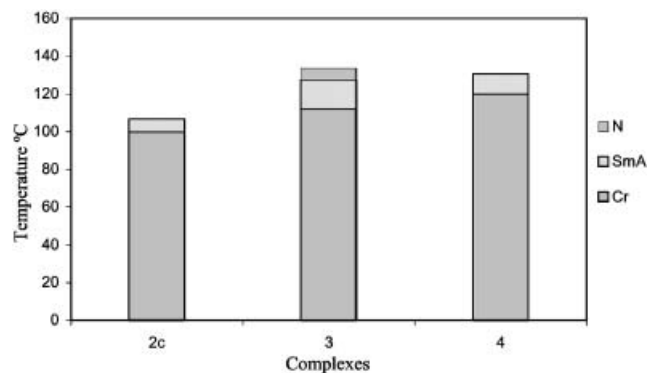


Figure 3. Plot of the mesomorphic behaviour for the H-bonded complexes **2c**, **3** and **4**.

Table 2. Transition temperatures and enthalpy changes for the complexes between 3-(4-pyridyl)-5-(4-*n*-octyloxy)phenyl-1,2,4-oxadiazole (**1c**) and (a) benzoic acid (complex **2c**), (b) 4-methylbenzoic acid (complex **3**) and (c) 4-chlorobenzoic acid (complex **4**): Cr=crystal, SmA=smectic A, N=nematic, I=isotropic.

Complex	Transition	Temperature/°C		Enthalpy/J g <sup>-1</sup> by DSC
		by POM	by DSC	
<b>2c</b>	Cr–SmA	99	99.7	41.0
	SmA–I	107	106.8	10.6
	I–SmA	104	104.9	–10.8
	SmA–Cr	99	98.8	–40.6
<b>3</b>	Cr–SmA	111	112.0	55.8
	SmA–N	128	127.5	3.8
	N–I	139	138.3	1.5
	I–N	137	137.2	–1.7
	N–SmA	127	126.4	–3.5
	SmA–Cr	110	109.7	–54.5
<b>4</b>	Cr–SmA	119	120.0	48.2
	SmA–I	132	131.5	8.4
	I–SmA	130	130.6	–8.7
	SmA–Cr	120	119.5	–46.8

Table 3. Results of the high temperature X-ray study of the mesophases of complexes **2c**, **3**, **4**. Parameter *d* represents the layer thickness in the smectic A mesophases or the length of the fluctuations in the nematic phase (see discussion in the text). Parameter *L* is the complex length estimated from Dreiding stereomodels for a fully extended conformation.

Complex	Temperature/°C	Phase	<i>d</i> /Å	<i>L</i> /Å
<b>2c</b>	102	SmA	30.5	34
<b>3</b>	120	SmA	30.5	35
	135	N	29.5 <sup>a</sup>	
<b>4</b>	127	SmA	32	34.5

<sup>a</sup>Diffuse maximum.

that there is no regular intermolecular distance inside the layers. This feature, as well as the orthogonal character of the mesophase, supports its smectic A nature.

It is interesting to note that the measured layer thickness *d* is slightly smaller than the estimated length *L*. Although theoretically the layer spacing in a smectic A mesophase would be expected to be equal to the molecular length, the value measured experimentally is usually smaller than that predicted from molecular models. This is due in most cases to the conformational freedom of the hydrocarbon chains in the mesophase (presence of a number of *gauche* bonds), as well as to the possibility of local fluctuations of the direction of the molecular axes, all of which can reduce the effective length.

With regard to the high temperature mesophase shown by complex **3**, the X-ray patterns confirm its nematic nature. The small angle reflection that is sharp and strong in the smectic A mesophase of the same

complex, transforms into a diffuse maximum located approximately at the same position. A small angle diffuse maximum is typically observed for nematic mesophases and corresponds to a mass density wave along the molecule long axis (short range smectic fluctuations). The periodicity of these fluctuations (*d* for the nematic phase, in table 3) has a value similar to the smectic layer thickness *d* for the same complex.

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