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Hydrogen-bonded complexes between mesogenic heterocyclic Schiff's bases and mesogenic 4-*n*-nonyloxybenzoic acid: mesomorphic behaviour, FTIR study and PM3 semi-empirical calculations

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A new series of intermolecular hydrogen-bonded complexes has been obtained using mesogenic 4-*n*-nonyloxybenzoic acid and mesogenic 5-(4-pyridyl)-2-(4-*n*-alkoxy)benzylideneamino-1,3,4-thiadiazole moieties. The thermal and phase behaviour of these complexes were studied by thermal microscopy and differential scanning calorimetry. Intermolecular hydrogen bonding was studied by FTIR spectroscopy, from crystalline to the isotropic state. A study by PM3 semi-empirical calculations is also described.

1. Introduction

Since 1989, when Kato and co-workers reported new liquid crystalline compounds obtained by intermolecular hydrogen bonding between a pyridine group and a carboxylic group, the hydrogen bond has been extensively used as a tool for the formation of monomeric and polymeric liquid crystals [1–5].

Mixtures of unlike hydrogen-bonded molecules producing liquid crystals frequently involve donor molecules derived from carboxylic acids and acceptor molecules from pyridine, 4,4′-bipyridine or stilbazoles; however, pyridine derivatives containing the 1,3,4-thiadiazole heterocyclic, to our knowledge, have never been reported as acceptor molecules in the formation of liquid crystals by hydrogen bonding. Inspection of the literature shows that such donor and acceptor molecules may or may not be mesomorphic alone. In both cases, however, and primarily for non-mesomorphic molecules, hydrogen bonding is responsible for the formation of liquid crystalline phases.

Previously [6], we have reported the synthesis and mesomorphic properties of a new series of Schiff's bases, 5-(4-pyridyl)-2-(4-*n*-alkoxy)benzylideneamino-1,3,4-thiadiazoles (C_nOBS), as proton acceptor. In this paper the complexation of C_nOBS with 4-*n*-nonyloxybenzoic acid (C_9OBA) as proton donor is studied systematically as a function of temperature and length of the alkyl chain of the Schiff's base (C_nOBS) molecules (from pentyloxy to decyloxy), and as a function of the composition of the binary mixtures; the complex is represented as C_9OBA/C_nOBS. The hydrogen bonding is also investigated by FTIR spectroscopy and semi-empirical molecular orbital method at PM3 level.

2. Experimental

2.1. *Preparation of the hydrogen-bonded complexes*

The hydrogen-bonded complexes were prepared by slow evaporation of a chloroform solution containing the required amounts of the H-bonding donor (C_9OBA, 2.5×10^{-4} mol) and acceptor (C_nOBS) moieties, followed by drying *in vacuo* at 60°C. Before evaporation, the solutions were stirred at room temperature for 24 h.

2.2. *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. DSC measurements were conducted on a Rheometric DSC-V calorimeter with a heating and cooling rate of 5°C min^{-1}. The apparatus was calibrated with indium.

2.3. *FTIR measurements*

FTIR spectra were obtained on a Nicolet 550 FTIR spectrometer, resolution 4 cm^{-1}. Samples for hydrogen bond study at room temperature were pressed tablets with KBr. The samples for hydrogen bond study at various temperatures were sandwiched between two NaCl crystal plates. The sandwiched samples were held on a hot stage, equipped with a temperature controller.

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2.4. *Computational method*

Calculations were performed by using PM3 [7] method implemented on Gaussian 94W series of programs [8]. *Ab initio* HF calculations were carried out using optimized structures at the HF/3-21G* level.

3. Results and discussion

3.1. *Materials*

The chemical structures of donor and acceptor moieties and hydrogen-bonded complexes are shown in figure 1. The series of Schiff's bases (C_nOBS) used in this work were synthesized according to the general procedure previously described by us [6].

In the pure state, the early homologues ($n = 5$–7) display monotropic liquid crystalline properties and the homologues with $n = 8$–10 show enantiotropic liquid crystalline behaviour [6]. The transition temperatures are given below (temperatures in °C):

$n = 5$ Cr 149.5 I (141) SmA (136.1) Cr
$n = 6$ Cr 149.3 I (149) SmA (129.1) Cr
$n = 7$ Cr 152.4 I (150) SmA (129.1) Cr
$n = 8$ Cr 147.5 SmA 160.8 I
$n = 9$ Cr 141.9 SmA 163.3 I
$n = 10$ Cr 142.1 SmA 165.6 I.

The 4-*n*-nonyloxybenzoic acid (C_9OBA) used in the present work was synthesized as described elsewhere [9]. In the pure state this compound exhibits liquid crystalline behaviour—Cr 94.7 (94) SmC 118.9 (117) N 144.6 (143) I—transition temperatures in parentheses refer to reported data [10]. This is due to dimerization through intermolecular hydrogen bond leading to a lengthening of the rigid-rod moiety, which in turn induces liquid crystallinity [11, 12]. The existence of thermotropic mesophases stemming from hydrogen bond formation is well known in the case of 4-alkyl and 4-alkoxybenzoic acids [3, 13].

3.2. *Binary mixtures between C_9OBA and C_nOBS and their thermal and phase behaviour*

A series of H-bonded complexes was prepared using a varying mol % of C_9OBA, as a proton donor, and C_{10}OBS as a proton acceptor. Also, 1 : 1 stoichiometric H-bonded complexes were made from C_9OBA and each member of the C_nOBS homologous series. The thermal properties are given in tables 1 and 2, respectively. A graphical representation of mesomorphic behaviour as a function of mol % of C_9OBA, and as a function of the number carbon atoms (C_n) in the lateral chain of C_nOBS are given in figures 2 and 3, respectively.

The mesogenic properties of the complexes were characterized [14] from textural observations by thermal microscopy under a polarizing microscope. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms.

As mentioned above, pure 4-*n*-nonyloxybenzoic acid (C_9OBA) exhibits smectic C (SmC, schlieren) and nematic (N, marble) mesophases; the Schiff's bases (C_nOBS) exhibit smectic A (SmA, focal-conic and mielinic) as the

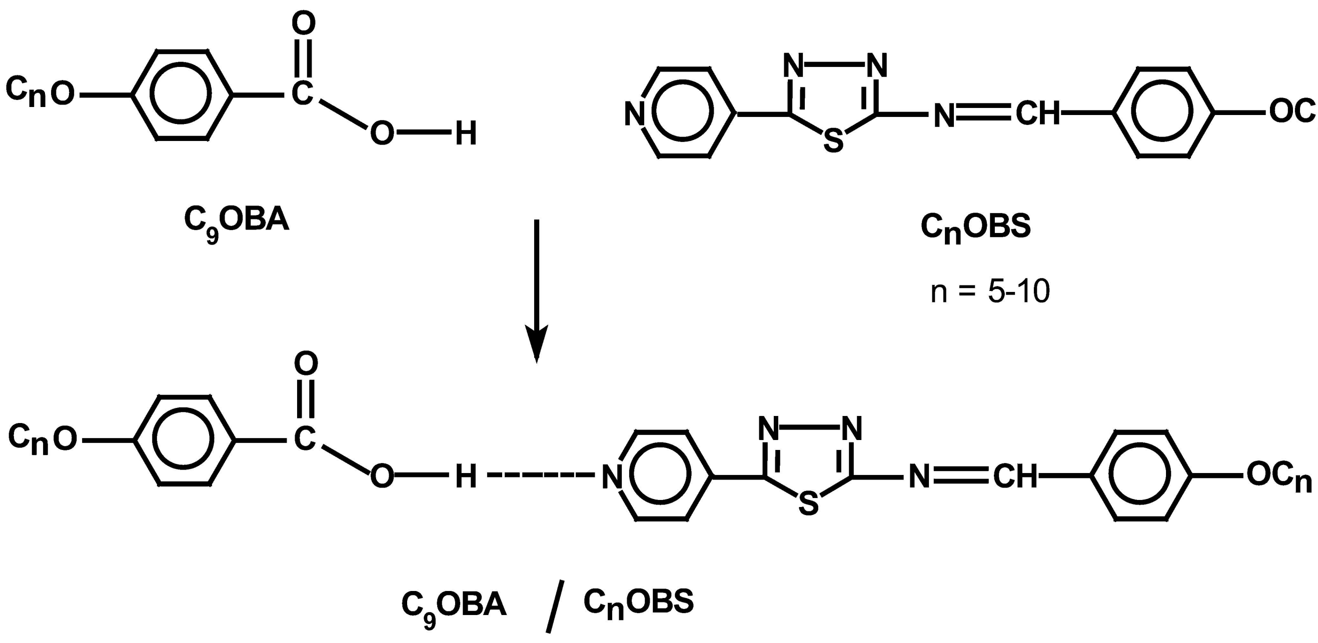

Figure 1. Representation of donor C_9OBA, acceptor C_nOBS ($n = 5$–10) and hydrogen-bonded complexes C_9OBA/C_nOBS.

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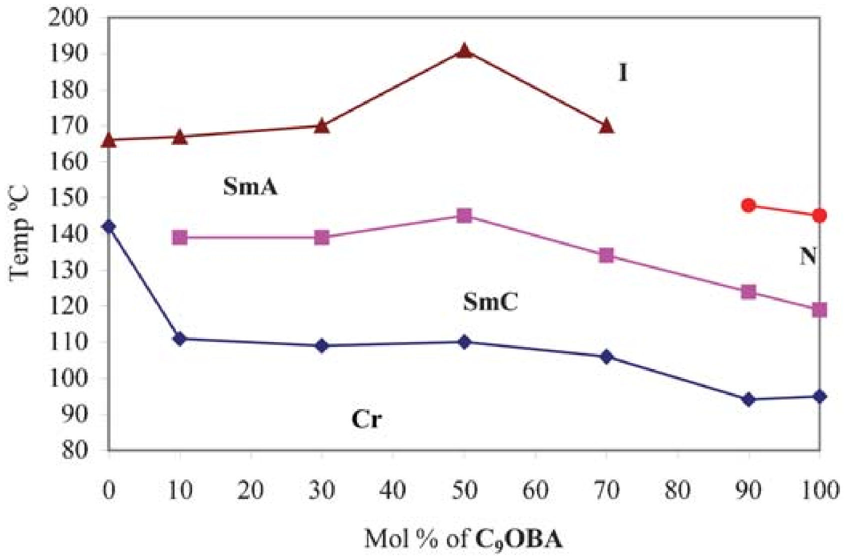

Figure 2. Plot of transition temperatures for binary mixtures (mol %) between C_9OBA and C_{10}OBS.

Table 1. Transition and thermal data for binary mixtures between C_{10}OBS and C_9OBA. Cr = crystal; SmC = smectic C; SmA = smectic A; N = nematic; I = isotropic.

C_9OBA, mol %	Transition	Temperature °C	ΔH/J g^{-1}
10	Cr–SmC	110.9	51.7
	SmC–SmA	139.3	[a]
	SmA–I	166.5	11.2
30	Cr–SmC	109.1	49.2
	SmC–SmA	139.0	[a]
	SmA–I	170.4	15.9
50	Cr–SmC	109.7	48.1
	SmC–SmA	145.3	[a]
	SmA–I	190.6	17.1
70	Cr–SmC	105.9	40.9
	SmC–SmA	133.7	[a]
	SmA–I	170.3	18.9
90	Cr–SmC	93.5	32.9
	SmC–N	124.0	[a]
	N–I	147.6	4.1

[a] The peak could not be detected.

unique mesophase, which is monotropic for homologues with $n = 5$–7 and enantiotropic for homologues with $n = 8$–10.

In the binary mixtures both the SmC and the SmA phases of the ligands are stabilized; however, in the C_9OBA/C_{10}OBS mixture, the melting point occurs at a lower temperature than that of pure C_{10}OBS, and at a higher temperature than that of pure C_9OBA. The clearing point occurs at a higher temperature and the mesophase stability range is broader than for the corresponding pure components, except for the mixture containing 90% of C_9OBA which presents the same mesophases and similar mesomorphic range to pure C_9OBA (see table 1 and figure 2).

Table 2. Transition and thermal data for the 1 : 1 hydrogen-bonded complexes between C_nOBS and C_9OBA (C_n: C_5–C_{10}). Cr = crystal; SmC = smectic C; SmA = smectic A; N = nematic; I = isotropic.

C_nOBS	Transition	Temperature °C	ΔH/J g^{-1}
C_5OBS	Cr–SmC	114.7	46.9
	SmC–SmA	136.8	[a]
	SmA–I	170.0	10.8
C_6OBS	Cr–SmC	114.2	47.5
	SmC–SmA	138.1	[a]
	SmA–I	172.2	11.9
C_7OBS	Cr–SmC	113.3	47.0
	SmC–SmA	140.1	[a]
	SmA–I	173.3	13.2
C_8OBS	Cr–SmC	112.1	47.3
	SmC–SmA	140.9	[a]
	SmA–I	180.1	14.8
C_9OBS	Cr–SmC	110.8	47.9
	SmC–SmA	142.5	[a]
	SmA–I	185.4	15.9
C_{10}OBS	Cr–SmC	109.7	48.1
	SmC–SmA	145.3	[a]
	SmA–I	190.6	17.1

[a] The peak could not be detected.

The 1 : 1 complex shows the highest clearing point and broader mesophase stability, suggesting that the interactions between C_9OBA and C_{10}OBS are particularly strong, and proving that a well defined 1 : 1 stoichiometric complex is formed, resulting from the hydrogen bonding of one Schiff's base molecule to one alkoxybenzoic acid molecule.

To generalize these observations, optical microscopy experiments were carried out with equimolar mixtures of 4-*n*-nonyloxybenzoic acid (C_9OBA) with a series of Schiff's bases (C_nOBS, $n = 5$–10). All the mixtures exhibit

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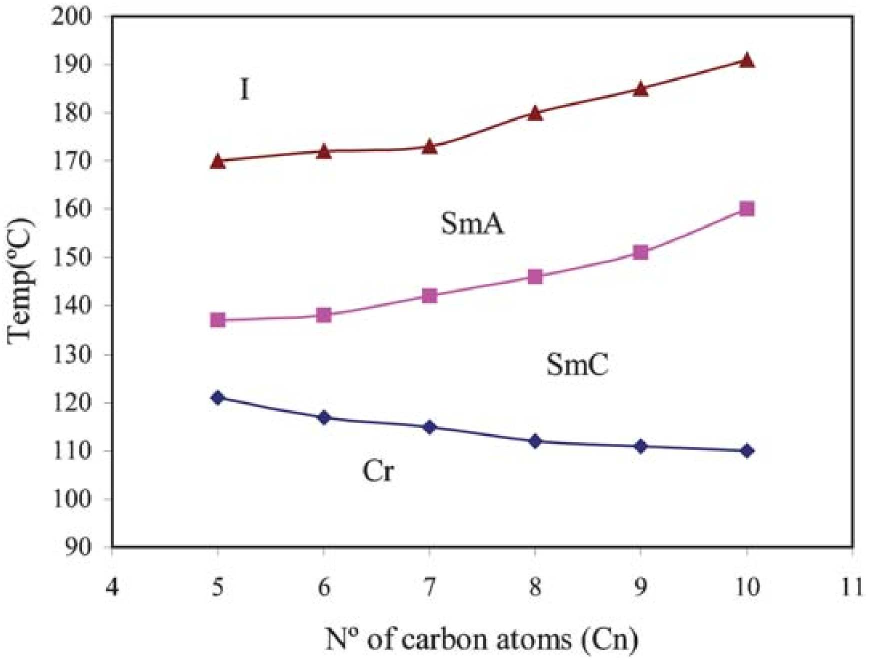

Figure 3. Plot of transition temperatures versus the number of carbon atoms (C_n) in the alkyl chain for the 1:1 hydrogen-bonded complexes C_9OBA/C_nOBS.

enantiotropic SmC and enantiotropic SmA phases. Quite clearly, the phases detected in the mixtures are exactly the same as those observed in the pure components, SmC in C_9OBA (the nematic phase is not present in the mixtures) and SmA in the corresponding pure C_nOBS. The significant difference is that the SmA phase obtained in all the mixtures is perfectly stable (enantiotropic), whereas the corresponding pure homologues of the C_5OBS–C_7OBS show a monotropic SmA phase. These observations confirm that hydrogen bonding is responsible for the stabilization of the mesophases. Moreover, the lateral chains in the C_nOBS compounds also play an important role in the stabilization of the mesophases. The mesomorphic range increases as the number of carbon atoms in the alkoxy chain increases (see table 2 and figure 3).

The optical textures observed upon slow cooling from the isotropic melt clearly show the existence of two distinct liquid crystal phases. The orthogonal SmA phase was characterized by its typical focal-conic fan texture coexisting with the homeotropic alignment; the tilted SmC phase was characterized by its broken focal-conic fan texture and by the fine four-brush schlieren texture (see figure 4).

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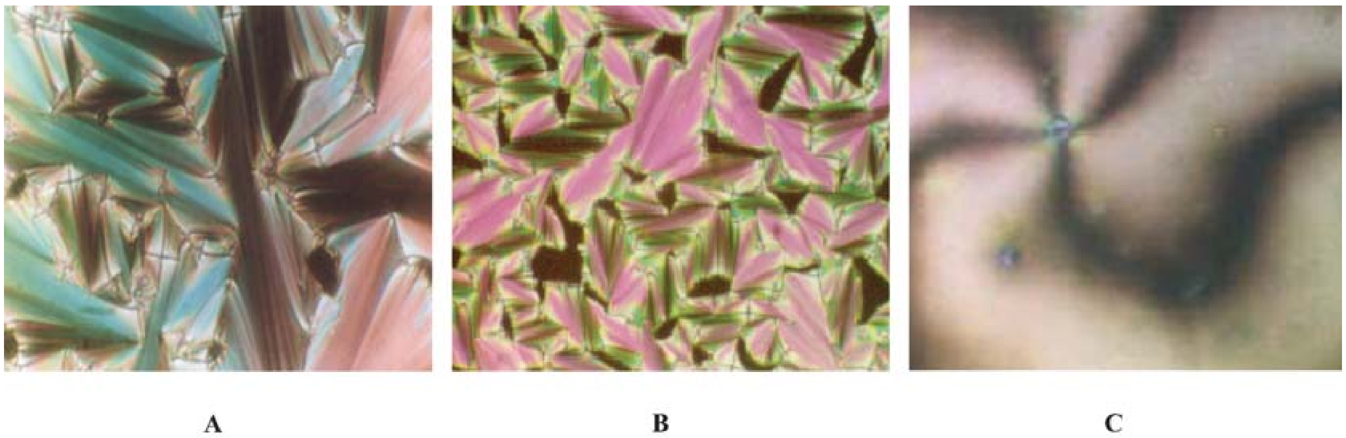
A **B** **C**

Figure 4. Mesophase textures of the C_9OBA/C_nOBS complexes obtained by cooling. (A) Focal-conic fan (SmA), (B) broken focal-conic fan (SmC), (C) schlieren (SmC).

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3.3. *Theoretical calculations at PM3 and HF/3-21G* levels*

The hydrogen bond plays a fundamental role in the mesomorphic properties of the C_9OBA/C_nOBS systems. The formation of strong hydrogen bonds is corroborated both from FTIR analysis (see § 3.4) and molecular orbital calculations. The FTIR spectrum of C_9OBA in the solid state shows typical bands in the carbonyl and hydroxyl regions, indicative of the acid dimer formation. However, in chloroform solution the equilibrium—acid dimer ⇔ acid monomer—is shifted toward the free form. Thus, in the presence of pyridine derivatives (C_nOBS) hydrogen bond formation between C_9OBA and C_nOBS will be possible if the interaction energy for this type of hydrogen bond is sufficiently large.

In this work, the PM3 semi-empirical molecular orbital method was used to evaluate the interaction energy of both the C_9OBA dimer and C_9OBA/C_nOBS systems [7]. We have used the C_1OBA and C_1OBS molecules as models. A total geometry optimization on both isolated structures and hydrogen bonding systems was performed. For comparison purpose we also carried out *ab initio* calculations at the HF/3-21G* level. We carried out calculations at the PM3 level since it has been shown PM3 and *ab initio* results are similar [15–17]. From a structural point of view PM3 shows improvement over other semi-empirical methods, for example AM1, especially when it is applied to the study of intermolecular interactions [16].

Table 3 shows the results obtained, at PM3 and HF/3-21G* levels, for the hydrogen bonding interaction in the C_1OBA dimer and the C_1OBA/C_1OBS system. The hydrogen bonding distances for C_1OBA ($r_{O...H}$) and C_1OBA/C_1OBS ($r_{N...H}$) are less than the sum of their respective van der Waals radii [18]; thus, in these systems a potential hydrogen bonding can be assumed [19]. The calculated hydrogen bond energies for the C_1OBA dimer is -4.4 kcal mol^{-1} for each hydrogen bond, while the hydrogen bond energy for C_1OBA/C_1OBS is -4.0 kcal mol^{-1}. Therefore, at the PM3 level the two systems have comparable hydrogen bond energies. The same tendency was found at the HF/3-21G* level; however, the energy values reported in table 3 are largely overestimated due to basis set superposition error [20]. The PM3 calculations also show that the charge transfer from donor to acceptor molecules take values between 0.055 and 0.025 units of charge for the C_1OBA dimer and the C_1OBA/C_1OBS system, respectively. These values of charge transfer should be associated with a strong hydrogen bond formation [17].

In addition to the hydrogen bonding energy, we investigated the effect of hydrogen bonding on the IR frequencies of C=O and O–H stretching modes. The shifts calculated, at the HF/3-21G* level, for C=O and O–H vibrations for the acid dimer are 87 and 635 cm^{-1}, respectively, to lower frequencies than the corresponding monomer. While for C_1OBA/C_1OBS, the frequency shifts are 51 and 460 cm^{-1}, respectively. Therefore, the frequency shifts of C=O and O–H characteristic modes are higher for the acid dimer than for the C_1OBA/C_1OBS system. The same trend was observed in the experimental studies.

Table 3. Hydrogen bond geometry and interaction energy for C_1OBA dimer and C_1OBA/C_1OBS system at PM3 and HF/3-21G* levels.

System[a]	PM3	HF/3-21G*
C_1OBA dimer		
$r_{O...H}$	1.773	1.606
$r_{O\text{–}H}$	0.967	1.001
$r_{O...O}$	2.740	2.601
$\angle_{O...H\text{–}O}$	178.6	171.6
ΔE/kcal mol^{-1}	-4.4	-14.2
C_1OBA/C_1OBS		
$r_{N...H}$	1.797	1.733
$r_{O\text{–}H}$	0.974	1.001
$r_{N...O}$	2.765	2.729
$\angle_{N...H\text{–}O}$	172.3	173.6
ΔE/kcal mol^{-1}	-4.0	-17.7

[a] r distances in Å and $\angle$ angles in degrees.

3.4. *FTIR measurements*

To evaluate the importance of hydrogen bonding in the formation of the liquid crystals investigated in the present work, binary mixtures of the Schiff's bases C_nOBS with 4-*n*-nonyloxybenzoic acid C_9OBA, were studied systematically by infrared spectroscopy. Firstly, the IR spectra of C_9OBA were investigated, both in the solid (KBr) and dissolved states, using various concentrations of chloroform solution at room temperature. From these studies we determined the concentration at which the dimeric C_9OBA completely dissociates into the monomeric form; this concentration was then used in the formation of the binary mixtures. The infrared frequencies (only pertinent bands) and their assignments are summarized in table 4.

Table 4. FTIR spectral data of C_9OBA in solid state and in varying concentrations of $CHCl_3$ solution.

State	$\nu_{C=O}$/cm^{-1}	ν_{OH}/cm^{-1}
Solid (KBr disk)	1680	3000, 2690, 2555
Solution 2.5×10^{-2} M	1685, 1730	3000, 2690, 2555, 3529
2.5×10^{-3} M	1685, 1730	3529 (sharp)
2.5×10^{-4} M	1730	3529 (sharp)

The solid state spectrum of 4-*n*-nonyloxybenzoic acid (C_9OBA) shows a sharp band at 1680 cm^{-1}. Furthermore, a very broad and strong OH band centred at 3000 cm^{-1}, along with two bands at ~2690 and 2555 cm^{-1}, which are considered to be Fermi resonances, are observed; these three bands characterize the acid dimer [5, 21–23].

In the dissolved state an additional sharp band at 1730 cm^{-1} (C=O) appears in the spectra, suggesting a gradual dissociation of the acid dimer with release of the free monomeric form. At the same time, the band at 1680 cm^{-1} due to the $\nu_{C=O}$ in the acid dimer, decreases in intensity to vanish completely beyond 2.5×10^{-4} M concentration (this concentration was used in the preparation of the binary mixtures). On the other hand, the two bands at 2690 and 2555 cm^{-1}, along with the very broad and strong OH band centred at 3000 cm^{-1}, diminish in intensity and a sharp and strong intense band appears at 3529 cm^{-1} which is assigned to the ν_{OH} mode of the acid monomer. It is of interest to note that the alkoxybenzoic acids in the pure state are completely dimerized at room temperature [3] and start to dissociate into single molecules only when heated to relatively high temperatures, essentially in the isotropic state or by dissolution in appropriate solvents.

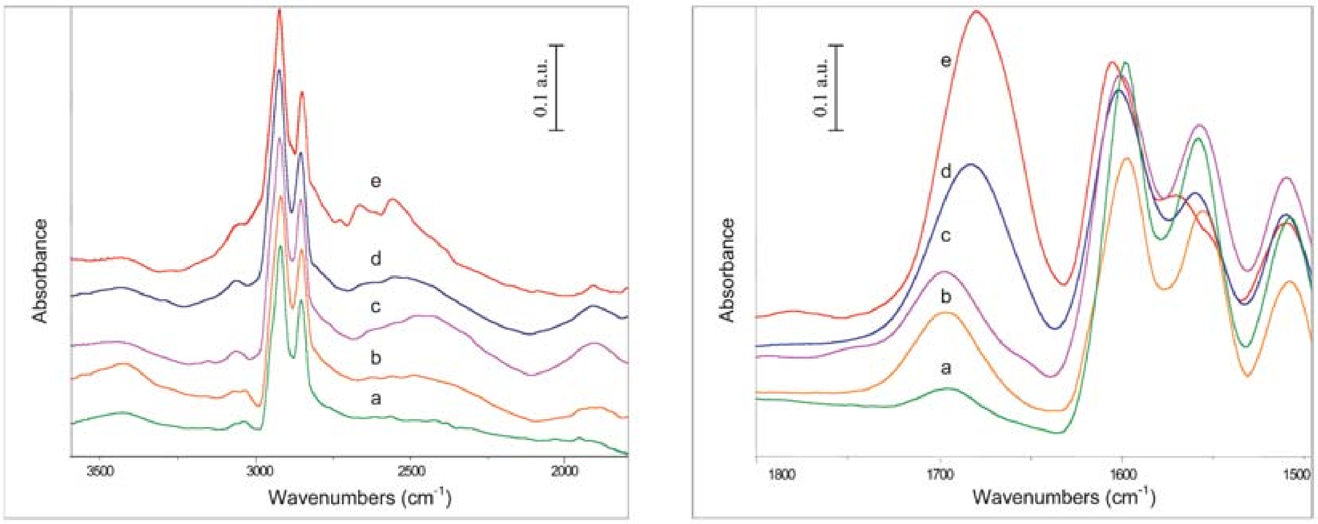
Secondly, the infrared spectra at room temperature of C_9OBA/C_{10}OBS mixtures at different mol % of C_9OBA were investigated (see figure 5). At room temperature, the infrared spectra of the crystalline mixtures show distinct features and changes depending on composition.

The carbonyl band at 1680 cm^{-1} corresponding to pure C_9OBA is replaced by the carbonyl band at 1698 cm^{-1}, suggesting the formation of the H-bonded complex between the pyridyl group of the Schiff's base (C_{10}OBS) and the OH group of the carboxylic acid. In the complexes the carbonyl group has a higher carbonylic character than in the corresponding acid dimer, so their band is shifted to higher frequencies.

In the mixtures with 10, 30, and 50 mol % C_9OBA, the band at 1698 cm^{-1} is the unique carbonyl band. Above 50 mol % C_9OBA the carbonyl band is separated into two bands at 1698 and at 1682 cm^{-1} (observed by deconvolution experiment) indicating the existence of two state of the carbonyl group; therefore in the mixtures of 70 and 90 mol % C_9OBA both the H-bonded complexes and the C_9OBA dimer are present. These results suggest that the C_9OBA present in the mixtures is engaged entirely in the formation of a stoichiometric 1 : 1 complex.

On the other hand, two additional broad bands at 1930 and 2440 cm^{-1} appear in the spectra, indicating strong hydrogen bonding of the pyridine ring of the C_{10}OBS with the carboxylic group of the acid (C_9OBA) [24–26]. Their intensity passes through a maximum for 50 mol % C_9OBA, pointing to the formation of a 1 : 1 complex between the Schiff's base C_{10}OBS and the benzoic acid C_9OBA. At the same time the characteristic bands of the acid dimer at 2690, 2555 and 3000 cm^{-1} disappear completely in the mixtures with 10, 30 and 50 mol % C_9OBA.

In order to examine the stability of the intermolecular H-bonding, the infrared spectra of the 1 : 1 complex (C_9OBA/C_{10}OBS) have also been recorded on heating from 110 to 200°C (see figure 6). The carbonyl band of



A **B**

Figure 5. Infrared spectra (KBr disk) of C_9OBA/C_{10}OBS mixtures at various C_9OBA mol % at room temperature. C_9OBA mol %: 10 (*a*), 30 (*b*), 50 (*c*), 70 (*d*), 90 (*e*). A: O–H, B: C=O.

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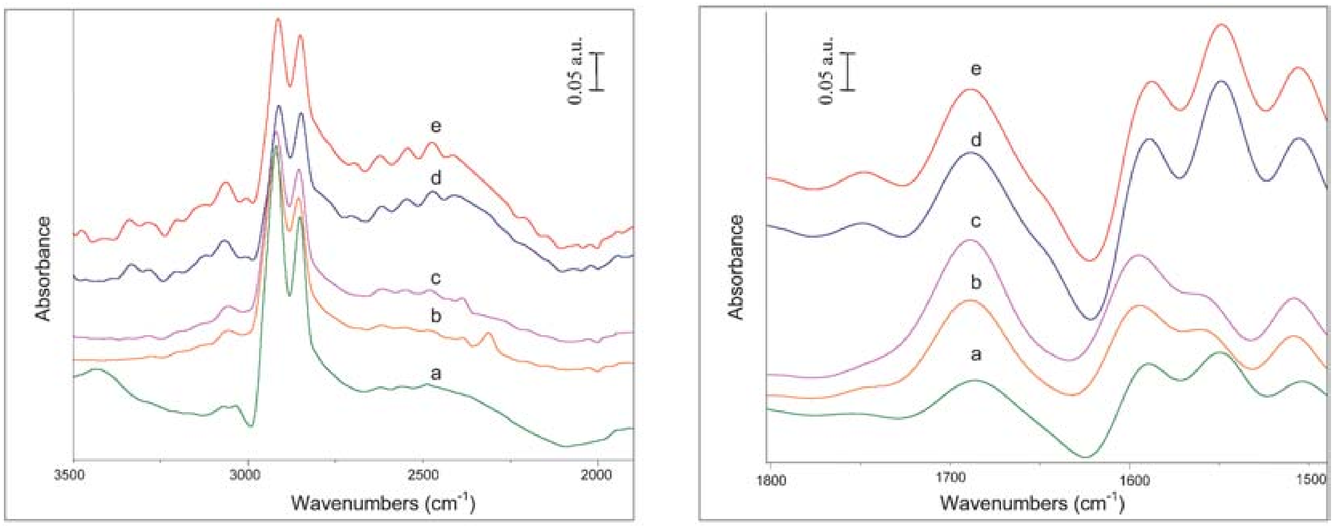

A **B**

Figure 6. Infrared spectra (NaCl crystal plates) of the 1 : 1 complex $C_9OBA/C_{10}OBS$. Temperature °C: 22 (*a*), 110 (*b*), 140 (*c*), 170 (*d*), 200 (*e*). A: O–H, B: C=O.

the 1 : 1 complex in the solid state (at 22°C) appears at ~1690 cm^{-1}; it increases in intensity on raising the temperature from 22°C to above the melting point. This carbonyl band is formed by overlapping of $\nu_{C=O}$ bands of the acid dimer and 1 : 1 complex. Also, a faint band at ~1730 cm^{-1}, characteristic of the acid monomer, appears in the spectra. These observations suggest a partial dissociation of the complex once the isotropization temperature is reached. Clearly, the hydrogen bonding of the complex, even though broken to some extent, does persist in the isotropic liquid state.

4. Conclusions

Binary mixtures of the Schiff's bases (C_nOBS) with 4-*n*-nonyloxybenzoic acid (C_9OBA) were found to produce liquid crystalline phases over wide ranges of composition and temperature. In all cases the SmA and SmC phases shown by C_nOBS and C_9OBA in the pure state are stabilized in the binary mixtures. Because the stability range of liquid crystals as a function of composition is very important, it is noteworthy that the 1 : 1 complexes have the higher mesomorphic range.

The hydrogen bonding of the molecules was studied as a function of temperature using FTIR spectroscopy. In the crystalline state, the benzoic acid (C_9OBA) was found to interact quantitatively with the Schiff's bases (C_nOBS) to form well defined stoichiometric 1 : 1 complexes. On increasing the temperature above the melting point the complex started to dissociate slightly, with the release of C_9OBA in dimeric and monomeric forms. However, although the hydrogen bonding of the complex is partially dissociated, it does persist into the isotropic state.

These results offer new information for the design and formation of supramolecular mesophases based on intermolecular non-covalent interactions.

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