# The effect of a thiophene ring in the outer position on mesomorphic properties of the bent-shaped liquid crystals<sup>†</sup>

Václav Kozmík,<sup>a</sup> Petr Polášek,<sup>a</sup> Arnošt Seidler,<sup>a</sup> Michal Kohout,<sup>a</sup> Jiří Svoboda,<sup>a</sup> Vladimíra Novotná,<sup>\*b</sup> Milada Glogarová<sup>b</sup> and Damian Pociecha<sup>c</sup>

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Novel bent-shaped compounds with the naphthalene central core possessing an outer thiophene unit in the lengthening arm were synthesized. Mesomorphic behaviour of new materials was studied using optical polarising microscopy, DSC, and electrooptic methods. The structures of mesophases were identified by X-ray diffraction and the structural parameters established. In the case of the thiophene unit in one molecular arm (the phenyl in the opposite arm) we succeeded in obtaining mesogenic properties for all types of lateral substitutions on the central naphthalene core. All non-substituted compounds and materials with the central core substituted by  $CH_3$  or Cl exhibited the  $B_2$  phase. The  $B_7$  phase has been observed for all compounds with CN-substituted central core. Materials with the thiophene unit in both lengthening arms were not liquid crystalline except for the CN-substituted compound exhibiting the  $B_7$  phase. Mesomorphic properties of compounds with the thiophene are compared with those detected on analogous materials with the phenyl ring.

## Introduction

Bent-shape liquid crystals have attracted a broad interest as they exhibit polar smectic phases.<sup>1-4</sup> Among others, only few materials possessing a heterocycle in the central core have been investigated. While the bonding in the six-membered heterocycles<sup>5-9</sup> does not disturb the typical bend angle around 120°, materials based on 2,5-disubstituted 1,3,4-oxadiazole,<sup>10-14</sup> 1,2,4-oxadiazole,<sup>15</sup> 1,3-oxazole,<sup>16</sup> 1,3,4-thiadiazole<sup>12</sup> obviously represent the borderline between the calamitic and bent-shaped materials due to their increased bend angle. Recently in a conference contribution bent-shaped liquid crystals with a thiophene ring in the lengthening arms were shown,<sup>17</sup> however the five ring materials with a resorcinol and naphthalene-2,7-diol central core lost their mesogenic properties.

Herein we report for the first time a complete study of the bentshaped liquid crystals with a thiophene unit in the outer position based on laterally 1-substited naphthalene-2,7-diol. Unlike the commonly exploited materials the intended introduction of a 2,5disubstitued thiophene unit leads to a further bend (148°) into the molecular structure, which can substantially affect the supramolecular assembly, and thus, the mesomorphic properties of the studied materials. In addition, for synthetic reasons instead of the routinely used alkoxy terminal chain a simple alkyl group was joined to the thiophene, uniformly the  $C_{12}H_{25}$  alkyl group. In order to distinguish the influence of both the thiophene unit and the character of the terminal chain (alkyl *vs.* alkoxy) on the mesomorphic properties of the studied materials, both symmetrical dialkyl- and non-symmetrical alkyl-alkoxy-terminated materials were also studied.

# Experimental

## Synthesis

Synthesis of materials I-V was performed by a stepwise acylation of the X-substituted naphthalene-2,7-diol by the methodology described in the preceding papers.<sup>18,19</sup> Their molecular structure is shown in Scheme 1. Details of the synthesis and NMR spectra of all synthesized compounds are described in ESI.<sup>†</sup>

### Characterization

All materials were studied using DSC (Perkin–Elmer Pyris Diamond). The samples, 2–4 mg, were hermetically closed in aluminium pans and placed into a nitrogen atmosphere. Cooling and heating rates of 5 K min<sup>-1</sup> were applied. The texture observations were carried out on the planar samples (3 or 6  $\mu$ m) using the polarizing microscope Nikon Eclipse. We prepared the cells from the glass plates provided with transparent ITO electrodes with the area of 5 × 5 mm<sup>2</sup>. The glasses were glued together and mylar sheets were used as (a) spacers. The cells were filled in the isotropic phase. The temperature was stabilized with accuracy ±0.1 °C in the hot stage (Linkam) placed on the table of polarizing microscope. For some measurements the commercial cells provided with aligning layers were used. The free standing films were prepared by spreading melted material over a circular hole in a metal plate.

For dielectric measurements, we prepared the cells from glass plates evaporated by a non-transparent gold electrode. Due to

<sup>&</sup>lt;sup>a</sup>Department of Organic Chemistry, Institute of Chemical Technology, CZ-166 28 Prague 6, Czech Republic. E-mail: Jiri.Svoboda@vscht.cz; Fax: +420220444182; Tel: +420220444288

<sup>&</sup>lt;sup>b</sup>Institute of Physics, Academy of Science of the Czech Republic, Na Slovance 2, CZ-182 21 Prague 9, Czech Republic. E-mail: novotna@fzu. cz; Fax: +420286890527; Tel: +420266053111

<sup>&</sup>lt;sup>c</sup>Laboratory of Dielectrics and Magnetics, Chemistry Department, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland. E-mail: pociu@chem.uw.edu.pl; Fax: +48228221075; Tel: +48228221075

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Scheme 1 Structure of materials I-V.

their high conductivity the parasitic high frequency mode (which causes cut-off frequency for a measurement) that is present at about 1 MHz if the ITO electrodes are used, was shifted to the frequency of one order higher. With the cells provided with the gold electrodes weak high frequency modes could be studied. Dielectric properties were studied using Schlumberger 1260 impedance analyzer. The frequency dispersions were measured on cooling at a rate of about 0.2 K min<sup>-1</sup>, keeping the temperature stabilized during the frequency sweeps in the range of 10 Hz–1 MHz.

Small angle X-ray diffraction studies were performed using Bruker Nanostar setup (Cu K $\alpha$  line, cross-coupled Goebel mirrors, Vantec 2000 area detector) equipped with a heating stage allowing a temperature control with a precision of 0.1 K. The experiments were done in the transmission mode for the samples in Lindemann capillaries. For broad angle XRD studies a Bruker D8 GADDS was used (Cu K $\alpha$  line, Goebel mirrors, point beam collimator, HiStar area detector). The samples were prepared as droplets on the heated plate.

#### Results

#### Mesomorphic properties

DSC studies have been performed for all compounds, the phase transition temperatures and associated enthalpy changes are collected in Table 1. According to the type of aromatic core in the lengthening arm and alkyl or alkoxy chain, the compounds are arranged into five groups. Compounds with the thiophene ring and the alkyl chain in both lengthening arms are designated **I/X**,

**Table 1** Temperature of melting point, m.p., was indicated on the second heating.  $T_{MI-iso}$  is the phase transition temperature from the isotropic to the mesophase and  $T_{cr}$ , is the temperature of crystallization, both temperatures were detected on the second cooling.  $T_{MI-M2}$  is the temperature of the phase transition from mesophase M1 to M2 established from X-ray measurements, round brackets symbolize that the phase is monotropic. The temperatures are in °C and the corresponding enthalpies,  $\Delta H$ , in square brackets behind the corresponding temperature value, are in kJ mol<sup>-1</sup>. All thermographs were taken at a rate of 5 K min<sup>-1</sup>

	M.p. [Δ <i>H</i> ]	$T_{cr}$ [ $\Delta H$ ]	M2	T <sub>M1-M2</sub>	M1	$T_{M1\text{-}iso}$ [ $\Delta H$ ]
I/H I/CH <sub>3</sub> I/Cl I/CN II/H II/CH <sub>3</sub> II/Cl II/CN II/CN II/CN IV/CH <sub>3</sub> IV/Cl IV/CN V/CN V/CN	$\begin{array}{c} 156 \ [+ 42.3] \\ 135 \ [+ 47.4] \\ 113 \ [+ 29.1] \\ 110 \ [+ 30.0] \\ 152 \ [+ 34.3] \\ 136 \ [+ 42.4] \\ 125 \ [+ 31.0] \\ 96 \ [+ 10.1] \\ 133 \ [+ 12.8] \\ 132 \ [+ 19.9] \\ 95 \ [+ 17.1] \\ 75 \ [+ 10.3] \\ 163 \ [+ 25.0] \\ 136 \ [+ 24.1] \\ 129 \ [+ 22.4] \\ 94 \ [+ 14.8] \\ 140 \ [+ 27.1] \\ 138 \ [+ 20.9] \\ 121 \ [+ 24.1] \\ 68 \ [+ 16.7] \end{array}$	$\begin{array}{c} 155 \ [-9.3]\\ 114 \ [-0.5]\\ 105 \ [-9.2]\\ 91 \ [-22.0]\\ 145 \ [-3.2]\\ 115 \ [-7.8]\\ 115 \ [-6.4]\\ 62 \ [-12.0]\\ 117 \ [-11.9]\\ 112 \ [-9.3]\\ 86 \ [-16.0]\\ 73 \ [-8.3]\\ 142 \ [-27.7]\\ 117 \ [-19.8]\\ 98 \ [-15.2]\\ 81 \ [-8.2]\\ 125 \ [-26.5]\\ 117 \ [-17.1]\\ 91 \ [-4.4]\\ 58 \ [-7.9]\\ \end{array}$		115	$\begin{array}{c} \\ \\ B_7 \\ (B_2) \\ (B_2) \\ B_7 \\ B_2 \\ B_3 \\ B_2 \\ B_4 \\ B_5 \\ B_5$	$\begin{array}{c} 136 \ [-25.1]\\ 151 \ [-19.6]\\ 133 \ [-20.7]\\ 118 \ [-17.4]\\ 160 \ [-25.4]\\ 154 \ [-20.5]\\ 136 \ [-22.5]\\ 123 \ [-19.2]\\ 151 \ [-23.4]\\ 168 \ [-20.1]\\ 149 \ [-16.8]\\ 137 \ [-14.8]\\ 170 \ [-21.4]\\ 169 \ [-20.4]\\ 150 \ [-20.3]\\ 138 \ [-17.7]\\ 165 \ [-20.7]\end{array}$
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**X** stands for a type of substitution (X = H, CH<sub>3</sub>, Cl and CN). **II**/**X** or **III**/**X** are compounds with a thiophene unit in one lengthening arm and alkyl or alkoxy chain in the terminal chain of the other arm, respectively. To study the effect of thiophene in comparison with the phenyl ring we synthesized series **IV**/**X** and **V**/**X** with Ar = phenyl and alkyl or alkoxy chain in the opposite arm, respectively.

The typical DSC plots are presented for compounds I/CN, II/ CH<sub>3</sub> and V/H in Fig. 1a, 1b and 1c, respectively. Other DSC thermographs are in the ESI.<sup>†</sup> The mesomorphic behavior of all the new materials has been studied using optical polarizing microscopy, DSC and electro-optic measurements. The results of the DSC analysis and the phase assignment are summarized in Table 1. In several cases there is an incomplete crystallization and/or additional phase transition in the solid state and a discrepancy when comparing melting and crystallization enthalpy value. It can be seen that the introduction of the thiophene ring in both lengthening arms (materials I/X) leads to a destabilization of the mesomorphic behavior for some types of the lateral substitutions. Namely materials I/H, I/CH<sub>3</sub> and I/CI exhibited the crystalline phase only and the presence of the lateral cyano substituent I/CN resulted in the occurrence of the B7 phase in a broad temperature range. The materials of series II, III, IV and V possess the  $B_2$  phase for non-substituted compounds and with the substitution by CH<sub>3</sub> or Cl. For CN substitution the B<sub>7</sub> phase has been found. For compound IV/CN and V/CN an additional columnar phase has been observed below the B7 phase on cooling by X-ray measurements. This phase was designated as the  $B_7'$  phase and will be described in the next paragraph.



Fig. 1 Typical DSC plots for (a) I/CN, (b)  $II/CH_3$  and (c) V/H. The upper and lower curves show the second heating and cooling runs, respectively. The slopes are adjusted for convenience, phases are indicated.

Unfortunately, the phase transition between the  $B_7$  and  $B_7'$  phase in not recognizable by DSC and/or textural observation in the polarizing microscope.

The planar texture of the  $B_2$  phase appearing below the isotropic phase exhibits different textural features. The most frequently observed is a tiny texture. Besides, the dark lowbirefringent domains that appear can be distinguished by decrossing the polarizers for an angle of about 6 degrees, the contrast being interchanged in the clockwise and the anticlockwise rotation. These two types of textures can coexist (see Fig. 2 for **II/CI**). Under an electric field of about 10 V  $\mu$ m<sup>-1</sup> applied for several minutes both textures transform into a fan shaped texture (Fig. 3). After switching off the electric field the fans are dark, which indicates a low birefringence (see Fig. 3a), with the extinction parallel to the crossed polarizers direction. It corresponds to the SmC<sub>A</sub>P<sub>A</sub> state (chiral anticlinic antiferroelectric). Under a d.c. electric field the birefringence significantly grows (see Fig. 3b, c) and the extinction brushes rotate by an angle of about 45 degrees clockwise or anticlockwise, respective to the



Fig. 2 The planar texture in the  $B_2$  phase of **II/Cl** (a) at crossed polarizers, with the analyzer rotated by an angle of about 6 degrees (b) anticlockwise and (c) clockwise from the crossed position. The width of the figures corresponds to about 200  $\mu$ m.



**Fig. 3** The planar texture of the  $B_2$  phase after the electric field treatment for **IV/CH<sub>3</sub>** (a) without electric field and at electric field of about (b) 20 V  $\mu$ m<sup>-1</sup> and (c) 40 V  $\mu$ m<sup>-1</sup>. The width of the figures corresponds to about 250  $\mu$ m.

polarity. After switching off the field the dark texture with the extinction parallel to the direction of the crossed polarizers is restored (Fig. 3a). The virgin textures (Fig. 2) could be restored by heating the isotropic phase and subsequent cooling.

The profile of switching current exhibits two peaks per half cycle of applied voltage in the  $B_2$  phase for a low frequency a.c. field, which prove the antiferroelectric character of this phase (see Fig. 4 for methyl substituted **III/CH<sub>3</sub>** and Cl-substituted **III/**Cl, more profiles are in ESI†).



**Fig. 4** The switching current profile under a triangular a.c. electric field in the B<sub>2</sub> phase for (a) **III/CH<sub>3</sub>** at T = 120 °C and a frequency of 12 Hz and (b) **III/CI** at T = 115 °C and a frequency of 11 Hz.



Fig. 5 The three-dimensional graph of the imaginary part of permittivity *versus* the temperature and frequency for **III/CI**.

In dielectric spectroscopy studies a single weak mode is established in the  $B_2$  phase with the relaxation frequency of hundreds kHz, which decreases with decreasing the temperature (see Fig. 5). Using the gold electrodes the cut-off frequency was shifted to a megahertz region and thus the high frequency mode could be detected. The studied mode completely disappears in the isotropic as well as in the crystalline phases (Fig. 5) so that the observed mode can be ascribed as an antiferroelectric collective mode.

In the  $B_7$  phase existing for all cyano substituted compounds typical spiral nuclei have been observed in the vicinity of the



Fig. 6 The microphotograph of a planar texture shows the phase transition from the isotropic to the  $B_7$  phase for I/CN. The width of the photo corresponds to about 150  $\mu$ m.



Fig. 7 The free-standing films of the  $B_7$  phase for IV/CN. The width of the photo corresponds to about 100  $\mu$ m.

phase transition from the isotropic to the  $B_7$  phase on cooling (see Fig. 6 for I/CN). The free standing films form a specific texture (see Fig. 7 for IV/CN) similar to those observed in the  $B_7$  phase for other compounds.<sup>20</sup>

#### X-Ray studies

The structures of mesophases were identified using X-ray diffraction. The X-ray patterns recorded for I/H, I/CH<sub>3</sub> and I/CI confirmed a crystalline character and the absence of liquid crystalline phases. On the contrary, for all CN substituted compounds the X-ray pattern typical for a 2D lattice with an oblique cell<sup>21</sup> has been detected (Fig. 8). The strongest signal indexed as (01) corresponds to the molecular length. It suggests a high degree of lamellarization of the structure, which is characteristic for the B<sub>7</sub> phase.<sup>21</sup> The cell parameters for all compounds with the B<sub>7</sub> phase measured by X-ray are summarized in Table 2. For I/CN the *c* parameter as well as *a* parameter, which reflects the block length within its cross-section, decreases on cooling. The cell parameters of IV/CN differ only negligibly from those established for V/CN because the only change in the



**Fig. 8** X-Ray intensity *versus* the scattering angle for **I/CN** at  $T = 130 \degree \text{C}$  with corresponding Miller indices.

**Table 2** Parameters of the crystallographic unit cell measured by X-ray in the  $B_7$  phase for selected compounds at selected temperatures, *T*. For **IV/CN** and **V/CN** last two temperatures are in the  $B_7'$  phase

Comp.	<i>T</i> /°C	a/Å	c/Å	β (°)r.
I/CN	130	114.3	39.46	115.5
	120	108.1	38.50	112.8
	110	102.0	37.30	108.0
III/CN	140	153.7	40.5	114.3
	120	159.3	40.3	113.6
	100	163.8	40.2	114.6
IV/CN	160	195.2	39.4	93.5
	140	192.2	39.5	93.9
	120	190.9	39.5	93.7
	100	123.7	42.6	118.3
	80	119.6	42.6	120
V/CN	160	192.4	38.3	93.2
	140	192.6	38.4	92.9
	120	194.5	38.2	91.9
	100	198.9	37.7	92.7
	80	122	43.6	125.2
	70	119	43.9	126.9

molecule between IV/CN and V/CN is one oxygen atom (dodecyl and dodecyloxy chains, respectively). On the contrary, the structural parameters significantly differ (when) comparing I/CN with the thiophene unit in both lengthening arms and IV/CN with the phenyl rings in the corresponding position, both having the same type of dodecyl chains. For I/CN the length of the block (a parameter) is about 110 Å, which corresponds to a half of the value established for IV/CN or V/CN (a changes from 190 to 198 Å, see Table 2). Compound III/CN with one thiophene on one arm and the phenyl on the opposite arm exhibits a block length of  $a \sim 155$  Å on average between values established for I/CN and IV/CN. For compound IV/CN and V/CN another columnar phase designated as the  $B_7'$  phase has been observed on further cooling. The X-ray pattern of  $B_7'$  can also be fitted with oblique 2D unit cell, however, in  $B_7'$  phase *a* parameter is substantially smaller and c parameter only slightly higher in comparison with the  $B_7$  phase (Fig. 9).

For all compounds exhibiting the  $B_2$  phase the X-ray patterns exhibit sharp, commensurate small angle reflections and a diffuse scattering maximum in a wide angle region. It shows a lamellar structure with the liquid-like molecular packing within the layers and confirms the presence of the lamellar smectic  $B_2$  phase. From the small angle reflections the layer spacing, *d*, was evaluated. Temperature dependence of *d* is presented in Fig. 10 for III/H, III/CH<sub>3</sub>, III/Cl, V/CH<sub>3</sub>. For II/CH<sub>3</sub> *d* was found practically temperature independent with value of about 38.1 Å. The layer spacing is substantially smaller than the calculated molecular length, *l*, which is about 57 Å for example for II/CH<sub>3</sub>. Thus the



Fig. 9 Fitted parameters of the columnar lattice are shown for (a) IV/ CN and (b) V/CN.

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III/CH

V/CH



Fig. 10 Temperature dependence of the layer spacing, d, in  $B_2$  phase for indicated compounds.

38.4

tilt angle,  $\Theta$ , can be roughly estimated to be approximately 45 degrees. This value fits well to the angle of rotation of the extinction brushes from the crossed position when we observe the fan-shaped textures under the polarizing microscope (see above). The temperature dependence of the layer spacing reveals only small increase on cooling, which can be connected with a stretching of dodecyl or dodecyloxy chains (see Fig. 10 for **III**/**CI**). The identification of phases obtained from the X-ray study is in agreement with the results acquired from the texture studies.

## **Discussion and conclusions**

Influence of thiophene unit on mesomorphic properties of banana compounds with the central naphthalene core substituted with CH<sub>3</sub>, Cl or CN is studied. Properties of synthesized bent-shaped molecules are compared with those of similar compounds with phenyl instead of thiophene.

Introduction of the thiophene unit in both arms of the studied compounds (series IX) destroys mesomorphic properties for non-substituted as well as CH<sub>3</sub> and Cl substituted cores (X = H, CH<sub>3</sub>, Cl). It is probably due to the presence of an additional bend of molecule caused by thiophene units, which disturbs a close packing of molecules. Only CN substitution enforces the mesogenic behavior and the B<sub>7</sub> phase is stabilized in a temperature range 25 K above the melting point. It is the first bent-shaped mesogen with a thiophene in both arms. One can speculate why only bulky CN groups stabilize the mesomorphic properties for compounds with the thiophene unit in both arms.

In all compounds with the thiophene ring in one arm, regardless of substitution, the mesomorphic properties are preserved. For series **II/X** the monotropic  $B_2$  phase occurs for X = H,  $CH_3$ , Cl and a  $B_7$  phase is stabilized in a wide temperature interval for CN substitution. The situation is changed when the terminal alkyl chain is exchanged for alkoxy type (series **III/X**). Then the melting point lowers and thus the  $B_2$  phases for X = H,  $CH_3$ , Cl become enantiotropic.

When the thiophene is replaced by phenyl in both molecular arms (series IV/X and V/X differing in the alkyl/alkoxy chain) the phase transition temperatures become higher by 10 to 29 K, only the crystallization temperatures are not affected. Besides, the temperature range of the B<sub>7</sub> phase, occurring in the CN compounds, is in fact composed of two columnar B7-like structures not-distinguishable in DSC study and in the texture observation. The first order phase transition between them is established from temperature dependence of lattice parameters (Fig. 9). The role of alkyl/alkoxy groups in the terminal chain can be clarified for series IV/X and V/X. One can see the mesomorphic behavior of the related materials is uniform and presence of the alkoxy chains causes only a slight lowering of the melting point, changes in the clearing point and in the width of mesophases being nearly negligible. On the contrary, for series II/X and III/X with the thiophene ring in one arm the role of the type of the terminal chain (alkyl and/or alkoxy) is significant.

The presence of thiophene also influences structural parameters of the  $B_7$  phase, namely the length of blocks *a* (periodicity of smectic layer undulation). Without the thiophene (IV/CN) parameter *a* is nearly as twice as long than that of I/CN with thiophene in both molecular arms (see Table 2). Smectic layer undulation for compound **III/CN** with one thiophene is averaged between *a* values for **I/C** and **IV/CN**.

To sum up, for the first time we have successfully applied thiophene ring for design of new bent-shaped mesogens. Thiophene bent-shaped mesogens are a promising class of compounds for resonant X-ray scattering studies.<sup>22,23</sup> Due to the presence of the thiophene unit one can expect a better resolution of this experimental technique, which can determine a layer organization in the B<sub>2</sub> and B<sub>7</sub> phases in details.

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