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Diphenylthiophenes as central part for the design of bent-core liquid crystalline compounds

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ABSTRACT

New type of bent-core molecules based on the 2,5-diphenylthiophene and 3,4-diphenylthiophene central cores have been synthesized as potential liquid crystalline compounds. We have varied non-linear 2,5-diphenylthiophene molecular core as a potential source of central unit of bent-core mesogens and for the first time introduced 3,4-diphenylthiophene central core in the design of V-shaped liquid crystals. Unfortunately, no mesogenicity has been observed for the 3,4-diphenylthiophene-based compounds. The effect of the lateral substitution on the central thiophene in 2,5-diphenylthiophene derivatives has been investigated. We have succeeded in substantial decrease of transition temperatures and the nematic phase has been observed for several compounds.

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1. Introduction

The electron-rich aromatic system of thiophene has been broadly utilized in the design of versatile electronic materials [1]. Due to its shape, materials with non-linear molecular structures exhibit a broad variety of liquid crystalline (LC) phases. The thiophene [2–9], oligo- and polythiophenes [10–16] and fused thiophene systems [13,14,17–28] can create the molecular core, however, there are also examples of their positioning at the terminal part of LC molecules [29–32]. There are attempts to utilize the thiophene as a central unit for bent-core liquid crystalline compounds. The most frequently reported materials are based on 2,5-disubstituted thiophenes. To pronounce the bend, the thiophene unit was also enlarged by joining one of two benzene units into these positions creating 2-phenylthiophene [8,12,33–41] and 2,5-diphenylthiophene [42–47] central cores of liquid crystals, respectively. In addition, insertion of an acetylene linkage between the benzene and thiophene unit results in formation of bis(phenylethynyl)thiophene and further stiffening of the bend of such central units [44,46,48–53]. From the crystallographic data on 2,5-diphenylthiophene [54], the bend angle between the phenyl units was calculated to be about 148°. Although these materials are bent, phenylthiophene-based materials [2,8,13,14,33,35] exhibited various phases typical for calamitic liquid crystals (with characteristic rod-like shape of molecules). Chiral materials [39,40] showed sequences of chiral smectic phases. Analogously, three-ring 2,5-diphenylthiophenes

terminated with alkyl chains [43,45] were nematogenic and the extended five-ring systems [43] showed the nematic-smectic phase sequences.

The three-ring materials based on bis(phenylethynyl)thiophene and terminated with an alkyl and alkoxy chain exhibited formation of a nematic phase or were not mesogenic, respectively [44,46,47,50]. On the other hand, lengthening both arms by introduction of a further aromatic unit can create various five-ring materials, mesomorphic properties of whose were dependent on the lateral substitution in the central thiophene core. While ethylenedioxy-substituted compounds exhibited nematic phases only [53], for the bromo and cyano-substituted compounds nematic phases, for di, and tricatener materials N-SmC phase sequence, and for tetracatenar compounds, hexagonal columnar phases were detected, respectively [48,52].

From the general point of view, the shape of the molecule plays very important role for molecular packing and self-organization in liquid crystalline mesophases. Substitution of the central thiophene at different position modifies the overall molecular shape and the dipole moment, which influences the mesomorphic properties. Mesomorphic behaviour of rod-like molecules has been studied for a long time. On contrary to classical rod-shape, even achiral bent-core molecules can be packed in a chiral manner and ferro and antiferroelectric mesophases have been observed [55]. Recently, the central-core angle has been varied and V-shaped (or acute-angle) molecules prepared with rather small angle (<90°). In most cases, V-shaped molecules exhibit calamitic mesophases, for example SmA phase [56,57]. Recently molecules with V-shape have been also utilized as dopants to enhance the flexoelectric coefficient in LC mesophases [58].

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In our previous studies on thiophene compounds we have also investigated five-ring 2-phenylthiophene based materials [33]. These materials exhibited various calamitic phases, character of whose was modified by fluorine lateral substitution and type and length of the terminal chains. In continuation of this study, herein we present results of synthesis and physical studies of series of 5 and 7-ring bent materials based on the 2,5-diphenylthiophene. Furthermore, newly we introduce an isomeric 3,4-diphenylthiophene central core, where the bend angle between the phenyl ring amounts 71° . Bent materials with such a bend angle belong to the family of acute angle, U-shaped, and/or V-shaped liquid crystals, which usually exhibit calamitic liquid crystalline mesophases [56,57,59,60]. We studied diphenylthiophene core to check its applicability in the design of liquid crystalline materials. Furthermore, the role of lateral mono and disubstitution (bromo, butyl, phenyl and phenylethynyl) on mesomorphic properties has also been investigated.

2. Experimental

2.1. Synthesis

The target compounds of the series **I–IV** have been prepared by acylation of central bisphenols **1,2** with acids **3,4** in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and catalytic amount of 4-dimethylaminopyridine (DMAP), see the generalized Scheme 1, the character of substituents R^1 , R^2 is shown in Tables 1 and 2, respectively. The synthetic procedures for the preparation of lateral substituted cores and the target compounds of series **I–IV** and their characterization for physical investigation are described in detail in the Supplemental information file. The structures of the synthesized compounds are depicted in Fig. 1.

2.2. Experimental methods

Phase transition temperatures were determined by differential scanning calorimetry (DSC) using Perkin-Elmer 7 calorimeter (Perkin Elmer, Shelton, CT, USA). The compounds about 2–5 mg were hermetically sealed in aluminium pans and inserted into the calorimeter chamber, which was filled in with a nitrogen atmosphere during measurements. Temperature and enthalpy change values were calibrated on extrapolated onset temperatures and enthalpies for melting points of water, indium and zinc. Calorimetric measurements were performed on cooling/heating runs at a rate of 5 K min^{-1} .

Phases were identified from textures and their changes observed under a polarizing microscope. Sample cells were observed in the optical microscope Eclipse E600Pol (Nikon, Tokyo, Japan). The glass cells for

texture observation and electro-optical studies were prepared from glasses with ITO transparent electrodes ($5 \times 5 \text{ mm}^2$) separated by two mylar sheets, which were used to define the cell thickness (usually of about $3 \mu\text{m}$). The glass cells were filled with studied compounds in the isotropic phase by capillary action. The Linkam LTS E350 heating/cooling stage with TMS 93 temperature programmer (Linkam, Tadworth, UK) was used which enabled temperature stabilization within $\pm 0.1 \text{ K}$.

The permittivity was measured using a Schlumberger 1260 impedance analyser (Schlumberger, Houston, TX, USA) in the frequency range of 10 Hz–10 MHz, at stabilized temperatures in Linkam stage during frequency sweeps.

The x-ray diffraction studies were performed using Bruker Nanostar system with $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.5418 \text{ \AA}$), Vantec 2000 area detector, MRI TCPU H heating stage) working in the transmission mode and Bruker GADDS system ($\text{CuK}\alpha$ radiation, HiStar area detector) working in reflection mode. In both systems the temperature stability was 0.1 K . Powder samples (for Nanostar) were prepared in thin-walled glass capillaries (1.5 mm diameter), partially oriented samples for experiments in reflection were prepared as droplets on heated surface.

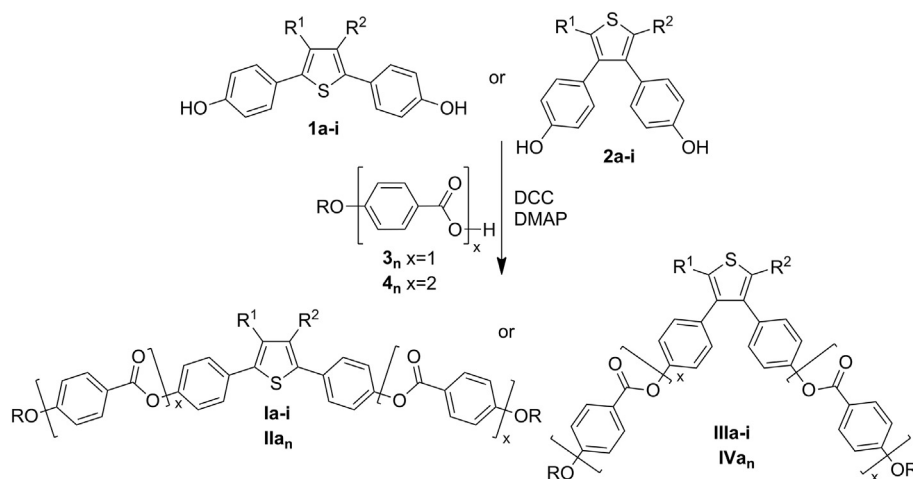
3. Results

3.1. Mesomorphic properties

DSC measurements were performed for all prepared compounds. As examples, DSC plots are presented for selected compounds **Ia₁₀**, **Ic** and **Ii** in Fig. 2. Phases were identified according their textures and textural changes under the polarizing microscope. Results of DSC analysis (phase transition temperatures and corresponding enthalpies) are summarized in Table 1. For selected compounds, x-ray scattering measurements were performed to confirm the phase identification (see later).

Compounds **Ia_n** represent five-ring mesogenic system without any lateral substitution of the core and exhibited a high-temperature N-SmC phase sequence. Prolongation of the terminal chain results in shortening the nematic to benefit of the SmC phase. For the dodecyl terminated compound **Ia₁₂**, the texture observed under polarizing microscope is presented in Fig. 3. Textures in the nematic phase revealed characteristic marble-like features (Fig. 3a) and in the SmC phase broken fan-shaped textures appeared on cooling below the N-SmC phase transition (Fig. 3b).

To investigate the influence of thiophene lateral substitution (R^1 , R^2), the length of the terminal chain in compounds **Ib–Ii** was set uniformly to dodecyl, $\text{C}_{12}\text{H}_{25}$. For bent-core molecules such a length often supports mesomorphic properties. Generally, introduction of a lateral



Scheme 1. Synthesis of materials **I–IV**.

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