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1,3-Dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives and their liquid crystalline difluoroboron complexes: Synthesis, characterization and comparative investigations of mesomorphic, thermotropic and thermo-morphologic properties

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HIGHLIGHTS

- Mesogenic barbituric acid difluoroboron complexes were synthesized for the first time.
- Effect of the chain length on mesomorphic properties has been found.
- Mesomorphic, thermotropic and thermo-morphologic properties have been investigated.
- Typical textures and microphotographs of the heterophase regions are presented.

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GRAPHICAL ABSTRACT

A series of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives and their difluoroboron complexes are synthesized. The mesomorphic, thermotropic and thermo-morphologic properties of these compounds were studied by POM, CTW and DSC techniques.



ABSTRACT

A series of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives **1a–4a** with various chain length were synthesized by our group for the first time through the addition of 1,3-dimethyl barbituric acid to 3,4,5-tris(alkoxy)benzoyl chloride at room temperature in presence of pyridine. For preparation of their difluoroboron complexes, the derivatives **1a–4a** reacts with borontrifluoride in the presence of triethylamine affording **1b–4b** in moderate yields. All derivatives and complexes have been fully characterized by MS, FT-IR and multinuclear NMR spectroscopy. We also explored their liquid crystal properties by using POM, OM, CTW and DSC techniques. The results show that **3b** and **4b** with longer alkyl chain are monomorphic mesogens and exhibited enantiotropic thermotropic liquid crystalline mesophases. Investigation of their mesomorphic, thermo-morphologic and thermotropic properties is presented in this work.

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1. Introduction

Liquid crystalline materials are the specific fluids which possess partial molecular orientational and positional ordering but have

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not the full translational symmetry as solid crystals. Liquid crystals are attracting considerable experimental, theoretical and applied interest for their fascinating physical and physico-chemical properties. These materials exhibit anisotropies in optical, electrical, magnetic, and viscous-elastic properties and display various types of structures, which are sufficiently sensitive to different external effects (temperatures, electric and magnetic fields, deformations,







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surfaces etc.) [1–5]. Therefore liquid crystals are important materials in scientific and engineering areas [3,6–9]. For example, these materials have been widely used in many practical applications such as photovoltaic solar cells [10], electroluminescent displays [11], electron transport systems [12], addressing systems [13], and thermography [14]. Because of the importance of molecular shape and size in the mesogenic structure, several studies deal with synthesis of new type mesogenic compounds [15–19]. β-diketonate complexes of boron compounds have been widely investigated in many different fields of material science because they show high stability in ambient air conditions. Especially their high luminescence quantum efficiency has led to useful applications for light emitting materials [20,21]. Recently the β -diketonate complexes of difluoroboron have been using for liquid crystals system. These species may solve some problematic issues in mesogenic optic nanomaterials because they combine luminescence properties and liquid crystallinity in the same compounds [22-26]. Other newly designed and synthesized liquid crystal systems have been reported to contain barbituric acid derivatives. Interestingly, although over many years a large number of liquidcrystalline compounds including heterocyclic moiety has been synthesized, there are very few examples of mesogenic barbituric acid derivatives [27-29].

While searching for novel mesogenic compounds for new applications in material sciences, we chose to target compounds featuring barbituric acid and difluoroboron groups. In this work we report our preliminary results, which are connected with the synthesis, characterization and liquid crystalline investigation of 1,3dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives and their difluoroboron complexes.

2. Experimental

2.1. Methods and samples

All procedures were performed under argon using standard Schlenk techniques. Commercially available reagents were used without further purification. 3,4,5-trialkoxy benzoyl chlorides (1–4) were prepared according to the reported procedures [30,31]. All reagents were purchased from Sigma Aldrich and used without further purification. Toluene was distilled over sodium and chloroform was distilled over calcium hydride before use. Melting points were measured with an Electro thermal 9200 melting point apparatus. ¹H, ¹³C NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. Chemical shifts are reported in ppm downfield from Me₄Si and were referenced to solvent peaks. Mass Spectra results were recorded on a Shimadzu LC-MS-8030 Triple Quadupole Mass Spectrometer. IR spectra were obtained on a Varian 900 FTIR spectrometer using KBr pellets.

The mesomorphic and thermo-morphologic properties have been studied by the polarizing optical microscopy (POM) technique using the trinoculer polarizing conoscopic/orthoscopic microscope, optical filters, compensators, λ -plates and microphotographic system from Olympus Optical Co., Ltd. and also special heater-thermostat with digital temperature control system. The POM is a sufficiently convenient and informative method for investigation of mesomorphic and morphologic properties of liquid crystals and also for identification of liquid crystalline mesophases. Morphologic and optical peculiarities of textures have been studied using the optical mapping (OM) technique [32,33]. This technique was applied for investigations of morphologic properties, peculiarities of specific and defective textures of liquid crystalline materials and identification of mesophases [34-37]. Studies of the thermotropic and thermo-optical properties of the heterophase regions of phase transitions have been carried out using the capillary temperature wedge (CTW) device. [38–41] The CTW provides, in a real scale of time and in a wide temperature range, an observation and study of all of the thermal states of liquid crystalline materials. The CTW also provides the calculation of the temperature widths of the biphasic regions with an accuracy of $\pm 10^{-2}$ and determination of the linear widths of these regions with an accuracy of $\pm 0.2 \times 10^{-3}$ mm [39,40]. The DSC-thermograms for phase transitions in materials under investigations were recorded on a Mettler TA 3000/DSC-30S with TA 72.5 software of Perkin–Elmer DSC-7.

2.2. Materials

2.2.1. General procedure for the synthesis of 1a-4a derivatives

A solution of 1,3-dimethyl barbituric acid (12.8 g, 0.1 mol) in 30 mL toluene/pyridine mixture (1:1) was added dropwise to a suspension of 3,4,5-tris(alkoxy)benzoyl chloride (0.1 mol) in pyridine (5 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. Then the mixture was poured into 8 M aqueous hydrochloric acid solution (250 mL). Resulting suspension was heated about 2 h at 70 °C and allowed to cool down to room temperature. The resultant precipitates were filtered, thoroughly washed with distilled water, dried and crystallized from 2-propanol.

2.2.1.1. 1,3-Dimethyl-5-(3,4,5-tris(octyl)benzoyl) barbituric acid **1a** derivative. Yield: 70%. ¹H NMR (400 MHz, CDCl₃): δ 17.65 (br, 1H, 0...H—O); 6.81 (s, 2H, —CH_{Ar}); 4.03 (t, *J_{HH}* = 6.4 Hz, 2H, —OCH₂—); 3.95 (t, *J_{HH}* = 6.4 Hz, 4H, —CH₂—); 3.42 (s, 3H, N—CH₃); 3.31 (s, 3H, N—CH₃); 1.73 (m, 6H, —CH₂—); 1.25–1.18 (m, 30H, —(CH₂)₉—); 0.84 (t, *J_{HH}* = 7.3 Hz, 9H, —CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.1, 171.3, 160.3, 152.6, 151.0, 142.7, 129.1, 108.7, 95.1, 73.8, 69.3, 66.1, 32.3, 32.2, 30.1, 30.0–29.5 (m, —CH₂—), 28.4, 28.2, 26.3, 26.2, 22.9, 14.6 ppm. FT-IR (KBr) v: 2953, 2919, 2846, 1725, 1695, 1557, 1247, 1119 cm⁻¹. MS (*m*/*z*): 644 (M+1).

2.2.1.2. 1,3-Dimethyl-5-(3,4,5-tris(decyloxy)benzoyl) barbituric acid **2a** derivative. Yield: 86%. ¹H NMR (400 MHz, CDCl₃): δ 17.63 (br, 1H, 0...H–O); 6.80 (s, 2H, –CH_{Ar}); 4.10 (t, *J*_{HH} = 6.4 Hz, 2H, –OCH₂–-); 3.97 (t, *J*_{HH} = 6.4 Hz, 4H, –CH₂–-); 3.43 (s, 3H, N–CH₃); 3.29 (s, 3H, N–CH₃); 1.78 (m, 6H, –CH₂–-); 1.23–1.16 (m, 42H, –(CH₂)₉–-); 0.88 (t, *J*_{HH} = 7.3 Hz, 9H, –CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.5, 170.9, 160.3, 152.7, 151.0, 142.3, 129.0, 108.5, 95.8, 73.7, 69.6, 66.1, 32.4, 32.2, 30.8, 30.3–29.8 (m, –CH₂–-), 28.5, 28.2, 26.1, 26.0, 22.7, 14.1 ppm. FT-IR (KBr) υ : 2949, 2916, 2843, 1723, 1693, 1555, 1243, 1115 cm⁻¹. MS (*m*/*z*): 729 (M+1).

2.2.1.3. 1,3-Dimethyl-5-(3,4,5-tris(dodecyloxy)benzoyl) barbituric acid **3a** derivative. Yield: 84%. ¹H NMR (400 MHz, CDCl₃): δ 17.67 (br, 1H, 0...H—O); 6.84 (s, 2H, —CH_{Ar}); 4.04 (t, *J_{HH}* = 6.4 Hz, 2H, —OCH₂—); 3.96 (t, *J_{HH}* = 6.4 Hz, 4H, —CH₂—); 3.43 (s, 3H, N—CH₃); 3.30 (s, 3H, N—CH₃); 1.77 (m, 6H, —CH₂—); 1.26–1.18 (m, 54H, —(CH₂)₉—); 0.88 (t, *J_{HH}* = 7.3 Hz, 9H, —CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.4, 170.6, 160.0, 152.6, 150.8, 142.5, 129.0, 108.3, 95.0, 73.9, 69.6, 66.1, 32.3, 32.2, 30.7, 30.5–29.5 (m, —CH₂—), 28.5, 28.4, 26.4, 26.2, 22.9, 14.4 ppm. FT-IR (KBr) υ : 2954, 2917, 2848, 1726, 1693, 1558, 1247, 1119 cm⁻¹. MS (*m*/*z*): 813 (M+1).

2.2.1.4. 1,3-Dimethyl-5-(3,4,5-tris(tetradecyloxy)benzoyl) barbituric acid **4a** derivative. Yield: 88%. ¹H NMR (400 MHz, CDCl₃): δ 17.62 (br, 1H, 0···H–O); 6.81 (s, 2H, –CH_{Ar}); 4.08 (t, *J_{HH}* = 6.4 Hz, 2H, –OCH₂–-); 3.93 (t, *J_{HH}* = 6.4 Hz, 4H, –CH₂–-); 3.41 (s, 3H, N–CH₃); 3.32 (s, 3H, N–CH₃); 1.76 (m, 6H, –CH₂–-); 1.25–1.17 (m, 66H, –(CH₂)₉–-); 0.87 (t, *J_{HH}* = 7.3 Hz, 9H, –CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.3, 170.5, 159.9, 152.5, 150.7, 142.6, 129.0, 108.1, 95.2, 73.7, 69.5, 66.2, 32.1, 32.0, 30.6, 29.9–29.0 (m, --CH₂--), 28.5, 28.2, 26.3, 26.1, 22.9, 14.3 ppm. FT-IR (KBr) υ : 2951, 2914, 2847, 1726, 1691, 1557, 1247, 1115 cm⁻¹. MS (*m*/*z*): 897 (M+1).

2.2.2. General procedure for the synthesis of **1b–4b** complexes

BF₃·Et₂O (2 mL, 8 mmol) was added dropwise to a solution of triethylamine (2 mL, 15 mmol) and **1a–4a** (0.8 mmol) in dry CHCl₃

70 mL at room temperature. After stirring for 5 h at the same temperature the reaction mixture was refluxed for 4 h. After quenching with water, the organic phase was separated and the aqueous phase was extracted with CHCl₃. The combined organic phases were washed with water, dried over anhydrous MgSO₄ and evaporated. The crude product was crystallized form toluene at -30 °C and give pure yellow solid.



Fig. 1. 1,3-Dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives 1a-4a.



1a- 4a

1b- 4b

Fig. 2. Difluoroboron complexes of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives 1b-4b.



Fig. 3. ¹H NMR spectra of 1,3-dimethyl-5-(3,4,5-tris(dodecyloxy)benzoyl) barbituric acid (a) and its difluoroboron complex (b).





Fig. 4. Microphotographs, connected with **1b** and **2b** derivatives. Crossed polarizers; magnification ×200. (a) typical texture of crystalline phase at 299.7 K; (b) heterophase region of the Cr – I phase transition; (c) heterophase region of the I – Cr phase transition.

2.2.2.1. Difluoroboron complex of 1,3-dimethyl-5-(3,4,5-tris(octyloxy)benzoyl) barbituric acid **1b** complex. Yield: 35%. ¹H NMR (400 MHz, CDCl₃): δ 6.93 (s, 2H, -CH_{Ar}); 4.12 (t, *J_{HH}* = 6.6 Hz, 2H, -OCH₂--); 3.87 (t, *J_{HH}* = 6.6 Hz, 4H, -CH₂--); 3.50 (s, 3H, N-CH₃); 3.32 (s, 3H, N-CH₃); 1.74 (m, 6H, -CH₂--); 1.37-1.18 (m, 30H, -(CH₂)₉--); 0.80 (t, *J_{HH}* = 6.9 Hz, 9H, -CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 188.5, 168.1, 158.2, 152.2, 150.7, 146.3, 126.4, 110.2, 93.6, 74.1, 69.5, 66.1, 32.1, 32.0, 30.6, 30.0-29.0 (m, -CH₂--), 28.4, 28.2, 26.2, 26.1, 22.9, 15.0 ppm. ¹¹B NMR (96 MHz, CDCl₃): δ = -0.82 ppm.

FT-IR (KBr) v: 2950, 2915, 2850, 1723, 1692, 1560, 1380, 1245, 1118 cm⁻¹. MS (*m*/*z*): 692 (M+1).

2.2.2.2. Difluoroboron complex of 1,3-dimethyl-5-(3,4,5-tris(decyloxy)benzoyl) barbituric acid **2b** complex. Yield: 45%. ¹H NMR (400 MHz, CDCl₃): δ 6.91 (s, 2H, -CH_{Ar}); 4.10 (t, *J_{HH}* = 6.6 Hz, 2H, -OCH₂--); 3.87 (t, *J_{HH}* = 6.6 Hz, 4H, -CH₂--); 3.49 (s, 3H, N-CH₃); 3.30 (s, 3H, N-CH₃); 1.74 (m, 6H, -CH₂--); 1.37-1.19 (m, 42H, -(CH₂)₉--); 0.80 (t, *J_{HH}* = 6.9 Hz, 9H, -CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 188.5, 168.0, 158.2, 152.1, 150.3, 146.2, 126.4, 110.1, 93.6, 74.0, 69.5, 66.0, 32.4, 32.1, 30.5, 30.2-29.3 (m, -CH₂--), 28.2, 28.1, 26.3, 26.0, 22.8, 15.1 ppm. ¹¹B NMR (96 MHz, CDCl₃): δ = -0.88 ppm.

FT-IR (KBr) v: 2950, 2919, 2850, 1725, 1695, 1561, 1381, 1246, 1117 cm⁻¹. MS (*m*/*z*): 776 (M+1).

2.2.2.3. Difluoroboron complex of 1,3-dimethyl-5-(3,4,5-tris(dodecyloxy)benzoyl) barbituric acid **3b** complex. Yield: 51%. ¹H NMR (400 MHz, CDCl₃): δ 6.94 (s, 2H, -CH_{Ar}); 4.14 (t, *J_{HH}* = 6.6 Hz, 2H, -OCH₂--); 3.89 (t, *J_{HH}* = 6.6 Hz, 4H, -CH₂--); 3.50 (s, 3H, N-CH₃); 3.33 (s, 3H, N-CH₃); 1.75 (m, 6H, -CH₂--); 1.39-1.19 (m, 54H, -(CH₂)₉--); 0.81 (t, *J_{HH}* = 6.9 Hz, 9H, -CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 188.6, 168.1, 158.4, 152.3, 150.8, 146.3, 126.5, 110.3, 93.7, 74.1, 69.6, 66.1, 32.2, 32.1, 30.6, 30.0-29.5 (m,

Table 1

Temperatures a	and	corresponding	enthalpies	of the	phase	transitions	for	3b	and 4	4b.
· · · · · · · · · ·										

Compounds	Transitions ^a	<i>Т</i> ^b (К)	ΔH (J/g)
3b	Cr—N	327.1	51.82
	N—I	344.2	17.76
4b	Cr—N	335.8	58.68
	N—I	342.0	14.32

^a Abbreviations: Cr = crystalline phase; N = nematic phase; I = isotropic liquid. ^b Onset temperatures obtained by DSC at heating rates of $10 \,^{\circ}\text{C}\,\text{min}^{-1}$ (He atmosphere). Values were taken from second heating run.

--CH₂--), 28.4, 28.3, 26.3, 26.2, 22.9, 15.2 ppm. ¹¹B NMR (96 MHz, CDCl₃): δ = -0.81 ppm.

FT-IR (KBr) v: 2955, 2918, 2849, 1726, 1693, 1560, 1382, 1247, 1118 cm⁻¹. MS (*m*/*z*): 861 (M+1).

2.2.2.4. Difluoroboron complex of 1,3-dimethyl-5-(3,4,5-tris(tetradecyloxy)benzoyl) barbituric acid **4b** complex. Yield: 60%. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (s, 2H, -CH_{Ar}); 4.11 (t, *J_{HH}* = 6.6 Hz, 2H, -OCH₂--); 3.87 (t, *J_{HH}* = 6.6 Hz, 4H, -CH₂--); 3.53 (s, 3H, N-CH₃); 3.32 (s, 3H, N-CH₃); 1.75 (m, 6H, -CH₂--); 1.37-1.19 (m, 66H, -(CH₂)₉--); 0.82 (t, *J_{HH}* = 6.9 Hz, 9H, -CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 188.7, 168.2, 158.3, 152.2, 150.8, 146.3, 126.5, 110.2, 93.6, 74.0, 69.6, 65.9, 32.1, 32.0, 30.6, 29.9-29.3 (m, -CH₂--), 28.3, 28.2, 26.3, 26.1, 22.9, 15.0 ppm. ¹¹B NMR (96 MHz, CDCl₃): δ = -0.82 ppm.

FT-IR (KBr) v: 2956, 2920, 2849, 1725, 1695, 1560, 1380, 1245, 1113 cm⁻¹. MS (*m*/*z*): 945 (M+1).

3. Results and discussion

3.1. Synthesis

1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives **1a–4a** were formed through the reactions of



Fig. 5. Typical textures of **3b** and **4b**, (a) texture of **3b** at 329.7 K (b) texture of **3b** at 338.7 K (c) texture of **4b** at 336.7 K and (d) texture of **4b** at 340.5 K. Crossed polarizers; magnification ×100.



Fig. 6. Sketch of the marble-like texture in uniaxial nematic mesophase.

1,3-dimethyl barbituric acid with 3,4,5-tris(alkoxy)benzoyl chloride (1–4) at room temperature in presence of pyridine. The reaction proceeded smoothly producing the corresponding

compounds in good yields. Indeed, according to FT-IR and ${}^{1}\text{H}$ NMR spectra: all of benzoyl barbiturates **1a–4a** can exist in enol–keto tautomers because of acidic hydrogen atom attached C-5 position [42] (Fig. 1).

In the next step when the 1,3-dimethyl-5-(3,4,5-tris(alk-oxy)benzoyl) barbituric acid derivatives **1a–4a** were treated with boron trifluoride diethyl etherate in presence of triethylamine, boron difluoride complex of 1,3-dimethyl-5-(3,4,5-tris(alkoxy) benzoyl) barbituric acid **1b–4b** were obtained in moderate yields. (Fig. 2).

All the compounds are air stable, nonhydroscopic and have been characterized by MS, FT-IR, ¹H, ¹³C and ¹¹B NMR spectroscopy. Spectroscopic data of the synthesized compounds are given in Section 2. An example of ¹H NMR spectra for **3a** and **3b** are shown in Fig. 3. The other ¹H NMR spectra of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives and their difluoroboron complexes were similar to that of **3a** and **3b** with the exception of the chemical shifts from the alkoxy groups.

The ¹H NMR spectra of compounds **1a–4a** revealed a broad peak at *ca.* 17.6 ppm which was readily assigned to OH protons. Therefore we infer that the enol forms are more preferable than keto



Fig. 7. N – I phase transition region in 3b (a) and 4b (b). Crossed polarizers; magnification ×200.



Fig. 8. Microphotographs of the heterophase regions of the I - N phase transition. 3b (a) and 4b (b). Crossed polarizers; magnification ×100.



Fig. 9. Texture of crystalline state of **3b** at 299.7 K. Crossed polarizers; magnification $\times 200$.



Fig. 10. Heterophase region of the *nematic mesophase* \leftrightarrow *crystalline state* phase transition for **3b**. Crossed polarizers; magnification $\times 100$.

forms in the solution due to an internal hydrogen bond (referred to as chelated enol) [42,43]. 3,4,5-tris(alkoxy)benzoyl- group shows a well defined singlet at *ca*. 6.8 ppm from aromatic proton. The aliphatic protons on the 1,3-dimethyl barbituric acid moiety appear at ca. 3.4 and 3.3 ppm. Examination of the ¹³C NMR spectra of **1a–4a** in CDCl₃ solution revealed that the chemical shift of the three carbonyl carbons have characteristic values at *ca*. 191, 170, 160 ppm [42,44].

The most significant changes between the ¹H NMR spectrum of the **1a–4a** and their boron complexes were absence of the resonance signal of hydroxyl protons at *ca*. 17.6 ppm. After complexation of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives with difluoroboron, ¹³C NMR signals shifted approximately 1–5 ppm to high field. ¹¹B NMR resonance at *ca*. 0.8 ppm is in agreement with the existence of a four coordinate boron atom [45].

In the Infrared spectra of all compounds, carbonyl stretching frequencies vary from *ca.* 1585 cm^{-1} to *ca.* 1705 cm^{-1} and some

of them are overlapped. The very strong bands in the range $2910-2840 \text{ cm}^{-1}$ can be attributed to C—H stretching associated with longer aliphatic chain.

In the case of **1a–4a**, we do not observed a broad peak in the *ca*. 3300–2600 cm⁻¹ region which possesses intramolecular H–bonding vibration. Therefore we can conclude that there is a shift of equilibrium to keto form in the solid state for **1a–4a** [46,47]. The most significant differences between the FT-IR spectra of the 1,3dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives and their boron complexes are B–O vibration at *ca*. 1380 cm⁻¹ [25].

3.2. Mesomorphic, thermotropic and thermo-morphologic properties

Investigations showed that, **1a**, **2a**, **3a**, **4a**, **1b** and **2b** compounds have not mesomorphic properties. We did not observe clear crystalline state and phase transition for **1a–4a**. However **1b** and **2b** compounds exhibit crystalline phase and display *crystalline state* – *isotropic liquid* (Cr – I) and *isotropic liquid* – *crystalline state* (I – Cr) phase transitions. Textures of crystalline phase for **1b** and **2b** compounds were very similiar. As an example, such texture for **2b** is presented in Fig. 4a. This texture consists of so-called spherulite formations. Spherulites represent three dimensional figures, which consist in radially arranged elongated color formations with sharp grain boundaries. By heating of the samples, these formations melted to isotropic liquid (Fig. 4b); by cooling of the samples, these formations arose again in isotropic liquid (Fig. 4c).

3b and **4b** complexes exhibit monomorphic mesomorphism and display enantiotropic nematic liquid crystalline mesophase. In these complexes the direct *crystal* – *nematic mesophase* – *isotropic liquid* and the reverse *isotropic liquid* – *nematic mesophase* – *crystal phase* transitions have been observed. Temperatures of these phase transitions are presented in Table 1.

Nematic mesophase in 3b and 4b complexes exhibit textures, which are presented in Fig. 5. As is seen Fig. 5, these textures are the marble-like textures and are specific for nematic mesophase [48–50]. Marble-like texture is mosaic texture and consists of separate regions with uniform alignment. In each region the director \vec{n} has strongly definite orientation, but different regions are characterized by different orientation of the director \vec{n} . As is seen in in Figs. 4 and 5, the color of different regions is different. This is due to a change of the birefringence from both in-plane and out-of-plane variation of the director \vec{n} . In Fig. 6 a sketch of such texture is presented. Optical investigations showed that the boundaries between separate uniform regions are the disclinations and the inversion walls. The disclinations and the inversion walls represent the places of texture, where the breaks of optical continuity of mesophase take place. Optical and morphologic investigations showed that some of these disclinations and walls were placed perpendicular to the reference surfaces of the sandwichcell, but others were placed tilted to these surfaces.



Fig. 11. DSC thermograms of compounds $\mathbf{3b}$ (a) and $\mathbf{4b}$ (b) on second heating process.

Thermo-morphologic investigations showed that in region of the *nematic mesophase* – *isotropic liquid* (N - I) phase transition in **3b** and **4b** complexes a lot of thread-like formations take place (Fig. 7a and b). The origin of these formations is connected with temperature gradient in the phase transition region. We would like to note that texture with the thread-like formations can be also observed sometimes in smectic C mesophase. However optical and morphologic properties of thread formations in smectic C mesophase and nematic mesophase is different because smectic C mesophase is optically biaxial and nematic mesophase is optically uniaxial.

In the cooling process in region of the *isotropic liquid* – *nematic mesophase* (I - N) phase transition in **3b** and **4b** complexes, droplets appear in isotropic liquid (Fig. 8a and b). During the cooling process these droplets increased in sizes, merged and formed the large regions of nematic mesophase. An appearance of the droplets is typical for nematic mesophase.

We would like to note that crystalline state in **3b** and **4b** complexes display texture with spherulites (Fig. 9). This texture is three dimensional and really resembles the texture observed for **1b** and **2b** complexes. For these complexes the clear *nematic mesophase* \leftrightarrow *crystalline state* phase transition has been observed (Fig. 10). As is seen in Fig. 10, in the heterophase region of this phase transition coexistence of low temperature phase (crystalline state) and high temperature phase (nematic mesophase) takes place.

DSC thermograms for phase transitions in 3b and 4b were shown in Fig. 11. The corresponding phase transition, temperatures and associated enthalpy changes (ΔH) of the transition were summarized in Table 1.

4. Conclusion

In this work the synthesis, characterization and investigation of the mesomorphic, thermotropic and thermo-morphologic properties of four novel 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl) barbituric acid derivatives as well as their difluoroboron complexes are presented. These materials were characterized by various spectroscopic techniques such as MS, FT-IR, ¹H, and ¹³C, ¹¹B NMR spectroscopy. The mesomorphic, thermotropic and thermo-morphologic properties of these compounds were studied by POM, CTW and DSC techniques. Liquid crystalline properties have been found in **3b** and **4b** compounds with longer alkyl chains. These complexes exhibit nematic mesophase in relatively large temperature interval and have phase transition temperatures at sufficiently low temperatures.

It is important to note that **3b** and **4b** complexes are one of rare examples of liquid crystalline materials, which contain the barbituric acid and difluoroboron groups. On the other hand, thermotropic properties of these complexes make such materials interesting objects from both fundamental and application points of view. Therefore, modifications of the structures and photo-physical properties of such materials, e.g. electronic absorption spectra and fluorescence spectra are under active investigation.

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