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Synthesis and Mesomorphism of 1,3-Benzenedicarboxylic Acid Derivatives

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Abstract—4-Methoxy-1,3-benzenedicarboxylic acid esters and 4-(4-hexyloxybenzoylamino)phenyl 1,3-benzenedicarboxylate, each containing five aromatic rings, were synthesized. The influence of the structure of the synthesized banana-like compounds on their mesogenic activity was examined.

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Much attention in chemistry of liquid crystals is given to synthesis of molecules having a bent shape, so-called banana-like molecules [1]. Such compounds can form a mesophase with ferroelectric properties and find use as components for liquid crystal displays, increasing their speed. Therefore, revealing a correlation between their structure and mesomorphic properties is a topical problem.

The central fragment of banana-like compounds is most frequently 1,3-disubstituted benzene containing the same or different functional groups. The side fragments include four to six aromatic or heteroaromatic rings linked by bridging groups (ester, azomethine, azoxy, double, or triple bond). Data on preparation of liquid crystal banana-like compounds with the amide linking group are lacking, whereas rodlike mesomorphic aromatic acid amides forming nematic and smectic phases have been reported [2]. There are data on rodlike and discotic liquid crystals forming complexes with lanthanides, e.g., on substituted Schiff bases [3, 4], β-aminovinyl ketones [5, 6], substituted diaza-18-crown-6 ethers [7]; some of such complexes exhibit luminescence properties. Complexes of lanthanides with banana-like liquid crystals have not been studied. The banana-like esters of 1,3-benzenedicarboxylic and 4-bromo-1,3-benzenedicarboxylic acids, described in the literature [8], have the structure that does not allow any complexing activity to be expected.

The goal of this study was to prepare 1,3-benzenedicarboxylic acid esters containing an amide group as the second linking fragment and 4-methoxy-1,3-benzenedicarboxylic acid esters, to examine their mesomorphism, and to evaluate their complexing power toward lanthanides.

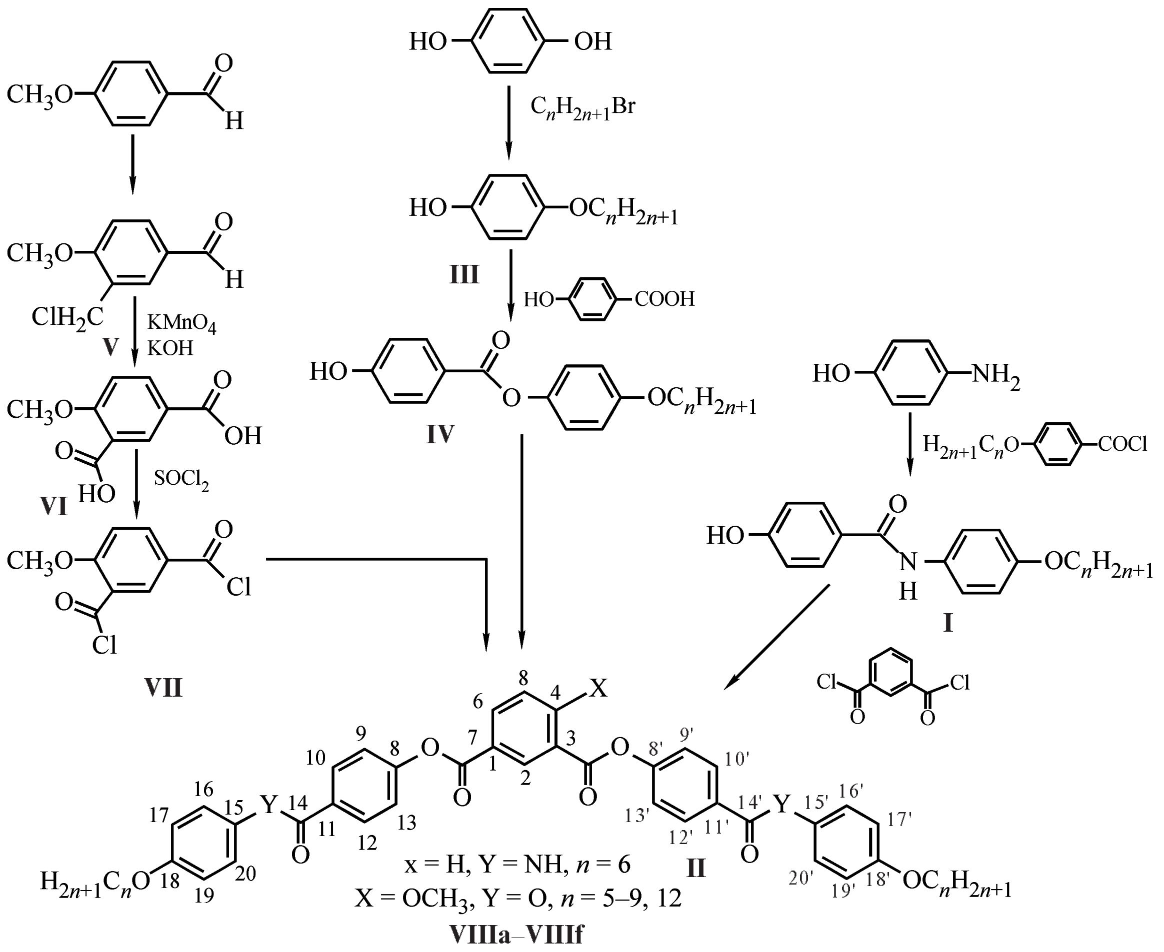
1,3-Benzendicarboxylic and 4-methoxy-1,3-benzenedicarboxylic acid derivatives were prepared by the scheme shown below.

Chlorides of 1,3-benzenedicarboxylic and alkoxybenzoic acids were prepared by the standard procedure [9] in thionyl chloride in the presence of DMF. *N*-(4-Hydroxyphenyl)-4-hexyloxybenzamide **I** was prepared by the modified procedure from [10]. Its structure was proved by mass spectrometry and IR spectroscopy ($\nu_{C=O}$ = 1680 cm^{-1}). 1,3-Bis[4-(4-hexyloxybenzoylamino)phenoxycarbonyl]benzene **II** was prepared in absolute acetone in the presence of triethylamine from isophthaloyl chloride and appropriate phenol **I**. Compound **II** shows no mesomorphic properties, has high melting point, and is very difficultly soluble in the majority of solvents.

Thus, introduction of an amide group as linker into side fragments of bent molecules negatively affects all the characteristics, including the mesogenic power. Therefore, we prepared 4-methoxy-1,3-benzenedicarboxylic acid derivatives containing exclusively ester groups in side fragments.

The starting 4-alkoxyphenols **III** were prepared by the procedure given in [11]. 4-(4-Alkoxyphenoxycarbonyl)phenols **IV** were prepared by esterification in the presence of sulfuric acid in anhydrous benzene [12]. The structures of phenols **IV** were confirmed by IR spectroscopy and mass spectrometry (Table 1).

4-Methoxy-1,3-bis[4-(4-alkoxyphenoxycarbonyl)-phenylene]benzenes **VIII** were prepared from the



corresponding phenols **IV** and 4-methoxy-1,3-benzenedicarbonyl chloride **VII** in absolute benzene in the presence of triethylamine at room temperature. The purity of compounds **VIIIa**–**VIIIf** was proved by thin-layer chromatography, and the structure, by ^{1}H NMR spectroscopy. The mesomorphic properties of the compounds were studied by polarization microscopy. The spectral and mesomorphic characteristics of 4-methoxy-1,3-benzenedicarboxylic acid diesters **VIIIa**–**VIIIf** are given in Table 2.

According to Table 2, compounds **VIIa** and **VIIIb** with short terminal alkoxy groups (n = 5, 6) and the highest homolog (**VIIIf**, n = 12) are nonmesomorphic; with the terminal heptyloxy group (compound **VIIIc**), a monotropic mesophase appears, which becomes enantiotropic for the next homologs **VIIId** and **VIIIe**.

To determine the kind of mesomorphism, along with studying the textures by polarization micros-

Table 1. Physicochemical characteristics of 4-(4-alkoxyphenoxycarbonyl)phenols **IV**

Compound	Yield, %	T_m, °C	IR spectrum, ν, cm^{-1}			M$^+$
			OH$_{ass}$	OH$_{free}$	C=O$_{ester}$	
IVa	25	163	3400	3600	1710	299
IVb	27	162	3400	3600	1700	313
IVc	69	167	3400	3600	1710	327
IVd	57	159	3360	3580	1700	341
IVe	53	152	3360	3580	1700	355
IVf	50	97	3360	3580	1705	397

Table 2. Properties of 4-methoxy-1,3-benzenedicarboxylic acid esters **VIIIa**–**VIIIf**

Compound	Yield, %	Found, %/Calculated, %		Empirical formula	^{1}H NMR spectrum, δ, ppm	Phase transition temperatures,* °C
		C	H			
VIIIa	60	70.7/70.8	6.3/6.2	$C_{45}H_{48}O_{11}$	0.89 t (6H, CH_3), 1.19–1.51 m (8H, CH_2), 1.7–1.86 m (4H, $OCH_2\mathit{CH}_2$), 3.95 t (4H, OCH_2), 4.07 s (3H, OCH_3), 6.93 d (4H, H-17, 19), 7.12 d (4H, H-16, 20), 7.17 d (1H, H-5), 7.38 d (2H, H-9', 13'), 7.40 d (2H, H-9, 13), 8.27 d (2H, H-10', 12'), 8.29 d (2H, H-10, 12), 8.43, 8.40 d.d (1H, H-6), 8.96 d (1H, H-2)	$Cr \xrightleftharpoons[149.4]{156.6} I$
VIIIb	58	71.2/71.4	6.6/6.7	$C_{47}H_{52}O_{11}$	0.88 t (6H, CH_3), 1.18–1.52 m (12H, CH_2), 1.7–1.85 m (4H, $OCH_2\mathit{CH}_2$), 3.95 t (4H, OCH_2), 4.07 s (3H, OCH_3), 6.94 d (4H, H-17, 19), 7.12 d (4H, H-16, 20), 7.18 d (1H, H-5), 7.38 d (2H, H-9', 13'), 7.40 d (2H, H-9, 13), 8.27 d (2H, H-10', 12'), 8.29 d (2H, H-10, 12), 8.43, 8.40 d.d (1H, H-6), 8.95 d (1H, H-2)	$Cr \xrightleftharpoons[150.6]{153.0} I$
VIIIc	64	71.7/71.5	6.8/6.9	$C_{49}H_{56}O_{11}$	0.88 t (6H, CH_3), 1.18–1.52 m (16H, CH_2), 1.7–1.86 m (4H, $OCH_2\mathit{CH}_2$), 3.95 t (4H, OCH_2), 4.08 s (3H, OCH_3), 6.93 d (4H, H-17, 19), 7.12 d (4H, H-16, 20), 7.18 d (1H, H-5), 7.38 d (2H, H-9', 13'), 7.40 d (2H, H-9, 13), 8.27 d (2H, H-10', 12'), 8.29 d (2H, H-10, 12), 8.43, 8.40 d.d (1H, H-6), 8.95 d (1H, H-2)	$Cr \xrightarrow{158.5} I$ $Cr \xleftarrow[152.0]{} B_x \xleftarrow[156.3]{} I$
VIIId	67.5	72.2/72.1	7.1/7.0	$C_{51}H_{60}O_{11}$	0.88 t (6H, CH_3), 1.18–1.52 m (20H, CH_2), 1.7–1.85 m (4H, $OCH_2\mathit{CH}_2$), 3.95 t (4H, OCH_2), 4.07 s (3H, OCH_3), 6.93 d (4H, H-17, 19), 7.12 d (4H, H-16, 20), 7.18 d (1H, H-5), 7.38 d (2H, H-9', 13'), 7.40 d (2H, H-9, 13), 8.27 d (2H, H-10', 12'), 8.29 d (2H, H-10, 12), 8.43, 8.40 d.d (1H, H-6), 8.95 d (1H, H-2)	$Cr \xrightleftharpoons[154.0]{154.0} B_x \xrightleftharpoons[167.0]{167.0} I$
VIIIe	63	72.6/72.7	7.3/7.2	$C_{53}H_{64}O_{11}$	0.87 t (6H, CH_3), 1.19–1.53 m (24H, CH_2), 1.7–1.86 m (4H, $OCH_2\mathit{CH}_2$), 3.95 t (4H, OCH_2), 4.07 s (3H OCH_3), 6.94 d (4H, H-17, 19), 7.12 d (4H, H-16, 20), 7.18 d (1H, H-5), 7.38 d (2H, H-9', 13'), 7.40 d (2H, H-9, 13), 8.27 d (2H, H-10', 12'), 8.29 d (2H, H-10, 12), 8.43, 8.40 d.d (1H, H-6), 8.95 d (1H, H-2)	$Cr \xrightleftharpoons[142.8]{148.0} B_x \xrightleftharpoons[157.1]{160.0} I$
VIIIf	62	73.7/73.9	7.9/7.8	$C_{59}H_{76}O_{11}$	0.89 t (6H, CH_3), 1.18–1.52 m (36H, CH_2), 1.7–1.86 m (4H, $OCH_2\mathit{CH}_2$), 3.95 t (4H, OCH_2), 4.07 s (3H OCH_3), 6.93 d (4H, H-17, 19), 7.12 d (4H, H-16, 20), 7.18 d (1H, H-5), 7.38 d (2H, H-9', 13'), 7.40 d (2H, H-9, 13), 8.27 d (2H, H-10', 12'), 8.29 d (2H, H-10, 12), 8.43, 8.40 d.d (1H, H-6), 8.96 d (1H, H-2)	$Cr \xrightleftharpoons{146.0} I$

* (*Cr*) Solid crystal, (*I*) isotropic liquid, and (B_x) "banana" mesophase.

copy (these textures for **VIIId** resemble a chiral smectic C* phase), we performed an X-ray diffraction study of the liquid crystal phase and differential thermal analysis [13].

In accordance with the X-ray diffraction data, the liquid crystal phase of **VIIId** is smectic, with the interlayer distance decreasing from 45.3 to 43.7 Å on cooling; the inclination angle of molecules relative to the layer surface reaches 12°–15°.

The thermogram of **VIIId** in the heating and cooling mode is shown in Fig. 1.

The heat of the crystal → mesophase transition (first peak in the heating mode) is 30.2 J g^{-1}, and the heat of the subsequent transition to the isotropic liquid is 12.6 J g^{-1}, which is typical of ordered smectic–isotropic liquid transitions. In the course of cooling, the isotrope → mesophase transition occurs at 159.0°C (17.2 J g^{-1}), and the crystallization (with supercooling), at 141.1°C (33.4 J g^{-1}). The data obtained suggest formation of a "banana" mesophase of modification B_1 or B_2.

We found experimentally that the reaction of a terbium salt with 4-methoxy-1,3-bis[4-(4-dodecyloxyphenoxycarbonyl)phenoxycarbonyl]benzene **VIIIf** yields a complex compound with the luminescence characteristic of Tb(III) ions. The reaction was performed by mixing a solution of terbium trichloride in methanol with a solution of the ligand in benzene. The complex exhibits fairly strong *f–f* luminescence caused by transitions in the Tb(III) ion from the excited $^5D_4$ level to sublevels of the ground ^7F_j level ($j \leq 6$).

Figure 2 shows the luminescence spectrum of the Tb(III) complex with **VIIIf** in which the lanthanide ion, most probably, is coordinated by oxygen atoms of the carbonyl and methoxy groups. The spectrum shows that the most intense luminescence of the Tb(III) ions in its complex with banana-like compound **VIIIf**, as in the majority of other Tb(III) complexes, is observed at 545 nm and is due to the $^5D_4$–$^7F_5$ hypersensitive transition.

EXPERIMENTAL

The ^{1}H NMR spectra of 5–10% solutions of the compounds were recorded on a Varian VXR-300 spectrometer operating at 300 MHz. The mass spectra were taken on an MKh-1321 spectrometer using the direct inlet system at an ionizing electron energy of 70 eV and ionization chamber temperature of 220°C. The IR spectra were recorded on a Specord IR-75 spectrophotometer in $CHCl_3$ solutions and KBr pellets. The luminescence spectra were measured on an SDL-1 spectrometer. The luminescence was excited with a DRSh-250 mercury quartz lamp. The radiation with wavelengths of 313 and 365 nm was cut out with light filters. The purity of the compounds prepared was evaluated by TLC on Silufol UV-254 plates in the 5 : 2 chloroform–acetone sys-

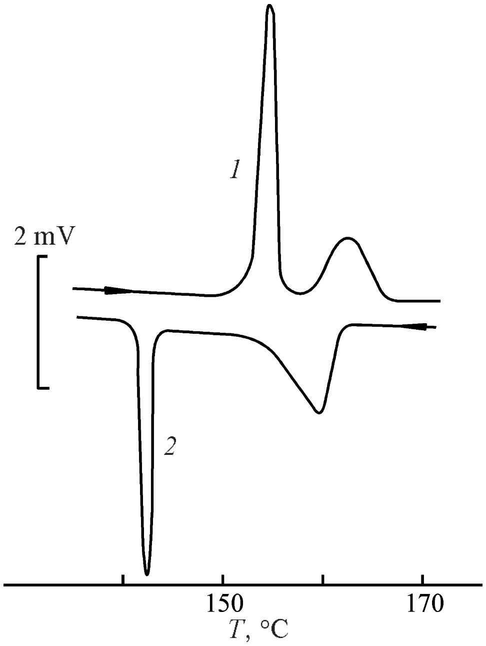


Fig. 1. DSC thermogram of 4-methoxybis-1,3-[4-(4-octyloxyphenoxycarbonyl)phenoxycarbonyl]benzene **VIIId**. (*T*) Temperature. (*1*) Heating and (*2*) cooling.

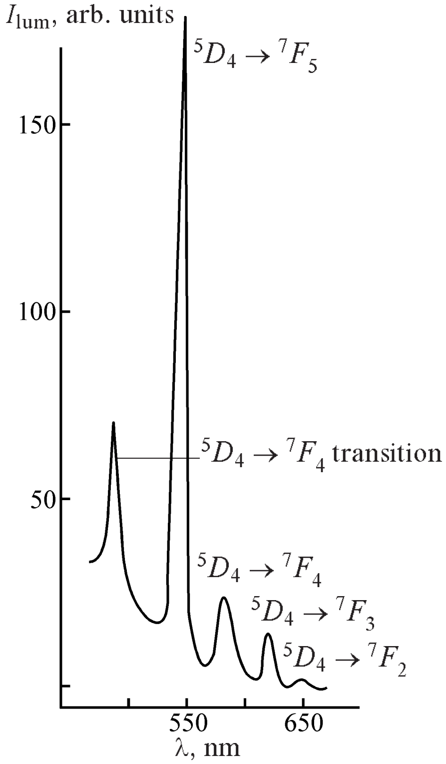


Fig. 2. Luminescence spectrum of the complex of Tb(III) with 4-methoxy-1,3-bis[4-(4-dodecyloxyphenoxycarbonyl)-phenoxycarbonyl]benzene **VIIIf**. $c_{Tb} = 1 \times 10^{-5}$, $c_{Lig} = 1 \times 10^{-4}$ M; 1 : 1.5 methanol–benzene solution. (I_{lum}) Intensity and (λ) wavelength.

tem. The spots were visualized by treatment with potassium ferricyanide and iron(III) chloride solutions. The phase transition temperatures of the compounds were determined by polarization microscopy on POLAM P-312 and Mettler TOLEDO FP 82HT microscopes (heating rate 3 deg min^{-1}).

4-Methoxy-1,3-benzenedicarboxylic acid was prepared in accordance with the procedures described in the literature; mp 270°C; published data [14, 15]: mp 270–271°C. The synthesis procedure and constants of chlorides of *p*-alkoxybenzoic and 1,3-benzenedicarboxylic acids are given in [16, 17]. 4-Dimethoxy-1,3-benzenedicarbonyl chloride (mp 79°C) was prepared in 68.7% yield by the standard procedure [9].

4-Hexyloxybenzoic acid 4-hydroxyanilide I. To a solution of 1.85 g (0.017 mol) of *p*-aminophenol in dimethylformamide (15 ml), 4 g (0.017 mol) of *p*-hexyloxybenzoyl chloride was added dropwise at room temperature. The mixture was left overnight. Then the mixture was poured into water (150 ml). The resulting crystalline precipitate was filtered off and washed with a large amount of cold alcohol. Yield 62%, mp 200–202°C. IR spectrum: $\nu_{C=O}$ 1680 cm^{-1}. Mass spectrum: M$^+$ 313.

Found, %: C 72.61, H 7.54, N 4.30.

Calculated, %: C 72.84, H 7.35. N 4.47.

1,3-Bis[4-(4-hexyloxybenzoylamino)phenoxycarbonyl]benzene II. To a solution of 0.812 g (0.004 mol) of isophthaloyl chloride in 8 ml of absolute acetone, we added simultaneously in portions 1.7 g (0.017 mol) of triethylamine and 2.6 g (0.0083 mol) of **I**. The mixture was refluxed for 4 h. The precipitate was filtered off, washed with water, and dried; mp 235°C. The compound is insoluble (even on heating) in alcohol, ether, chloroform, and 1 : 1 toluene–heptane mixture. The compound was refluxed in 1 : 1 acetonitrile–chloroform mixture, filtered off while hot, and dried; mp 243°C, yield 89%. IR spectrum, $\nu_{C=O}$, cm^{-1}: 1680, 1700.

Found, %: C 73.27, H 6.51, N 3.57.

Calculated, %: C 73.01, H 6.35, N 3.70.

4-Methoxybis-1,3-[4-(4-alkoxyphenoxycarbonyl)-phenoxycarbonyl]benzenes VIII. To a suspension of 0.0036 mol of phenol **IV** in 8 ml of absolute benzene, we added 0.8 ml of absolute triethylamine, after which we added dropwise a solution of 0.42 g (0.0018 mol) of chloride **VII** at 15°C and left at room temperature for 12 h. After the reaction completion (TLC monitoring), the suspension was poured onto a water (25 ml)–ice (25 g) mixture, carefully acidified with hydrochloric acid, and extracted first with ether (3 × 20 ml) and then with chloroform (3 × 20 ml). The extracts were washed with water to pH 7 and dried with anhydrous magnesium sulfate and calcium chloride. The solvents were removed under reduced pressure. The ether extract contained unchanged starting phenol **IV**. The residue after removing chloroform was recrystallized two times from a 4 : 1 alcohol–benzene mixture.

CONCLUSIONS

(1) Introduction of an amide group into side fragments of banana-like 1,3-benzenedicarboxylic acid esters leads to compounds showing no mesomorphism.

(2) Banana-like mesomorphic esters of 4-methoxy-1,3-benzenedicarboxylic acid were prepared. Their mesomorphic properties depend on the length of the terminal substituent, with the trend being similar to that observed for rodlike liquid crystals. Disappearance of the mesomorphism in the highest homolog with the terminal dodecyloxy group is due to twisting of the alkyl chain, which favors ordered packing of the molecules in a layer.

(3) The banana-like 4-methoxy-1,3-benzenedicarboxylic acid esters can be used as ligands for preparing a luminescent complex with the Tb(III) ion.

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