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Optically Active 4-(4-{4-[(2*S*)-(2-Methylbutoxy)]benzoyloxy}-phenyldiazenyl)benzaldehyde

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Abstract—4-(4-{4-[(2S)-(2-methylbutoxy)]benzoyloxy}phenyldiazenyl)benzaldehyde was synthesized and its structure was identified.

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Among the multitude of compounds exhibiting mesomorphism the class of thermotropic liquid crystals of cholesteric type is especially interesting. A unique property of these crystals to reflect selectively the light in the visible region makes them indispensable in designing modern temperature sensors for electronics and medicine [1, 2]. The possibility of local changes in optical properties of cholesteric mesogens under the action of light or electric field provides the opportunity to use them as photoactive materials for reversible (and irreversible) colored information storage in the systems possessing optical memory for display technology, photonics, optoelectronics, and holography [3]. A promising application of the mesophase of the cholesteric type is the analysis of the optical isomers of organic compounds by Gas Liquid Chromatography method [4].

Besides the individual compounds the chiral nematic phase may be formed of nematic mixtures either with cholesterol and chiral nematics or with optically active non-mesogenic additive. The number of chiral additives already synthesized for inducing helically stranded mesophase is fairly large [5–7].

We formerly synthesized, characterized supramolecular mesogenic 4-[4-(ω-hydroxyalkoxy)phenyldiazenyl]benzaldehydes, and investigated their mesomorphic properties [8]. 4-[4-(3-Hydroxypropoxy)phenyldiazenyl]benzaldehyde (**1**) exhibits polymorphism (Fig. 1) and is a highly efficient stationary phase for the gas chromatography [9].

In order to induce the chiral nematic phase in the mesophase of compound **1** we prepared optically

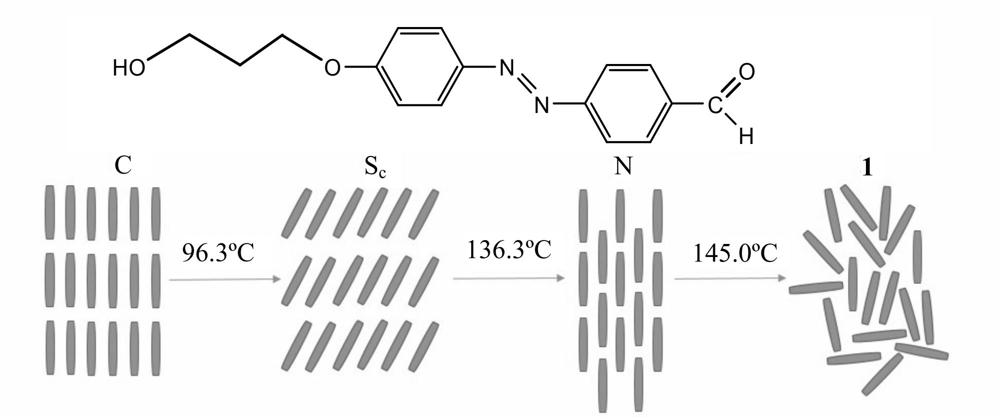
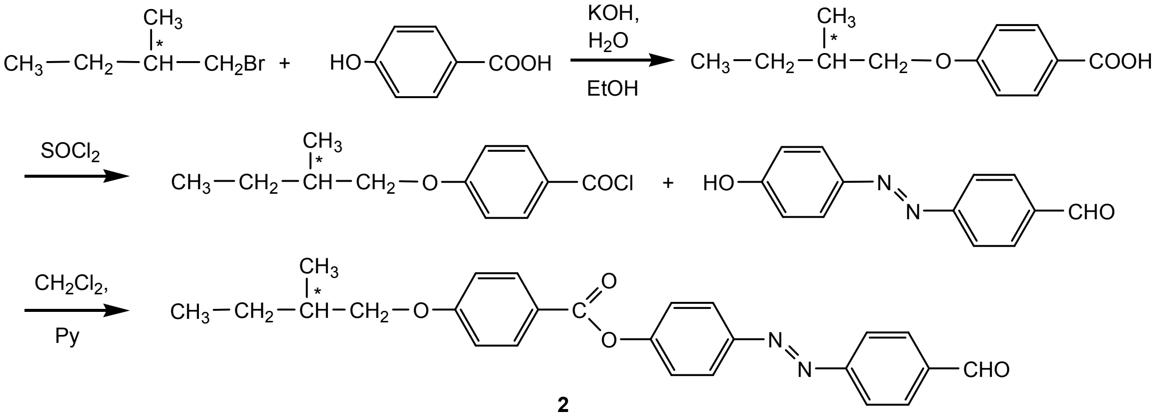


Fig. 1. Phase transition temperature of 4-[4-(3-hydroxypropoxy)phenyldiazenyl]benzaldehyde **1**.

Scheme 1.



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active 4-(4-{4-[(2*S*)-(2-methylbutoxy)]benzoyloxy}-phenyldiazenyl)benzaldehyde (**2**) by the condensation of 4-[(*S*)-2-methylbutoxy]benzoyl chloride [10] and 4-[4-(hydroxy)phenyldiazenyl]benzaldehyde [11] in dichloromethane in the presence of pyridine. The structure of compound **2** was established from ^{1}H NMR spectrum and elemental analysis (Scheme 1).

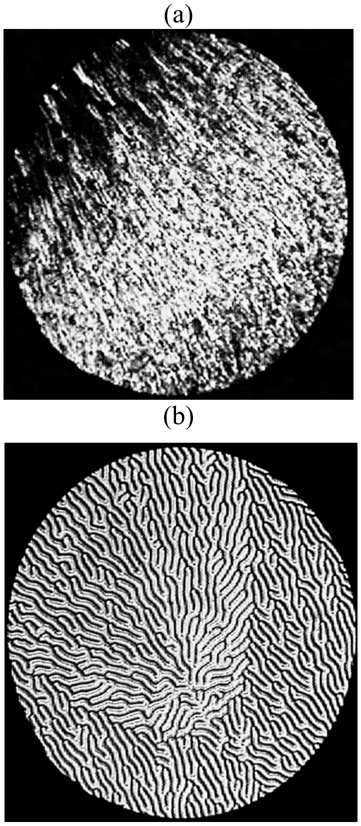
(a)
(b)

Fig. 2. Photo of textures of smectic (a) and chiral nematic (b) phases of the binary mixture of 90 wt % of supramolecular mesogen **1** and 10 wt % of optically active aldehyde **2**.

Note that mesogens **1** and **2** contain in their structure a reactive aldehyde group providing a possibility to perform the condensation of these compounds with pyrrole in order to prepare tetraphenylporphins for designing multipurpose functional materials underlain by macroheterocycles.

The polarization thermomicroscopic study was carried out on the optically active aldehyde **2** and the mixture containing 90 wt % of compound **1** and 10 wt % of aldehyde **2** obtained by stirring the components mixture in the isotropic liquid state over 1 h. It demonstrated that the synthesized aldehyde **2** possessed no liquid-crystalline properties; the mixture of aldehydes **1** and **2** at the mentioned components ratio melted at 91.0°C forming a smectic phase that at 121.8°C transformed into chiral nematic phase with a characteristic “finger prints” texture (Fig. 2). The transition of the binary system into the isotropic liquid state was observed at 143.0°C. Thus optically active aldehyde **2** induced a chiral nematic phase in the mesophase of the supramolecular liquid-crystalline compound **1** in a sufficiently wide temperature range.

EXPERIMENTAL

Recording of ^{1}H NMR spectra and measuring of the chemical shifts was performed on a high resolution spectrometer Bruker Avance III at operating frequency 500 MHz. The proton stabilization was carried out by $CDCl_3$. The chemical shifts were measured with respect to HMDS. The phase state of the synthesized mesogen and the binary mixture was studied using a microscope Polam P211 equipped with a heating block. The microscope was also equipped with a video camera KPC-S230CWX (3.6 mm) that made it possible to follow the dynamics of the phase transitions and to photograph the phase textures at any given moment. The temperature was measured with the accuracy ±0.1°C.

4-(4-{4-[(2*S*)-(2-Methylbutoxy)]benzoyloxy}-phenyldiazenyl)benzaldehyde (2). A solution of 1.31 g (5.8 mmol) of 4-[(2*S*)-2-butoxy]benzoyl chloride in 15 mL of dichloromethane was added dropwise to a solution of 1.3 g (5.8 mmol) of 4-[4-(hydroxy)phenyldiazenyl]benzaldehyde in 30 mL of dichloromethane and 5 mL of pyridine. The mixture was boiled for 12 h, cooled, then filtered, and the filtrate was evaporated. The residue was transferred into 150 mL of 3% solution of sodium hydrogen carbonate, the mixture was stirred for 1 h, then filtered, and the precipitate was washed with water. The reaction product was purified by recrystallization from hexane and ethanol. Yield 2.1 g (87%), orange-red bright crystals, mp 110.8°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, CH_3, *J* 7.48 Hz), 1.08 d (3H, CH_3, *J* 6.90 Hz), 1.32 q (1H, CH_2, *J* 6.90 Hz), 1.62 q (1H, CH_2, *J* 6.90 Hz), 1.93 m (1H, CH), 3.86 m (1H, OCH_2), 7.02 d ($2H_{Ar}$, *J* 8.70 Hz), 7.43 d ($2H_{Ar}$, *J* 8.70 Hz), 8.06 s ($4H_{Ar}$), 8.07 d ($2H_{Ar}$, *J* 7.50 Hz), 8.17 d ($2H_{Ar}$, *J* 8.70 Hz), 10.13 s (1H, CHO). Found, %: C 71.31; H 5.06; N 6.18. $C_{25}H_{24}N_2O_4$. Calculated, %: C 72.12; H 5.77; N 6.73.

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