

Mesogenic 4-[4-(ω -Hydroxyalkoxy)phenyl]diazenylcinnamic Acids and Their 4-Cyanophenyl Esters

S. A. Kuvshinova^a, D. S. Fokin^a, V. A. Burmistrov^b, and O. I. Koifman^b

^aIvanovo State University of Chemical Engineering, Ivanovo, Russia

^bInstitute of Solutions Chemistry, Russian Academy of Sciences, Ivanovo, 153460 Russia

e-mail: burmistrov@isuct.ru

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Abstract—Homologs of a series 4-[4-(ω -hydroxyalkoxy)phenyl]diazenylcinnamic acids (C₂, C₆, C₈, C₉, C₁₀) and their two 4-cyanophenyl esters (C₂, C₆) were synthesized. The substances obtained possess properties of thermotropic nematic liquid crystals. The effect of the terminal hydroxy group of the terminal substituent on their mesomorphous properties was analyzed.

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Liquid crystalline state of a substance combines a significant fluidity and long-range orientation order and consequently anisotropic physical characteristics. These qualities led to a wide application of mesogenic compounds in versatile fields of scientific research, in engineering, and technology [1]. The interest directed on mesogenic molecules with chemically active and polar terminal substituents (OH, CHO, CN, COOH) is caused by two reasons. Firstly, they can be readily subjected to chemical modification sharply extending the range of mesomorphous structures. Secondly, in the mesogenes formed by these molecules specific interactions may exist endowing them with new characteristics [2].

Besides a special interest attract heat-resistant liquid crystals because of their promising application to the analytical GLC as stationary phases for separation of high-boiling chemical substances, in particular, 3,4- and 3,5-lutidines, *p*- and *m*-cresol, naphthalene derivatives, polycyclic aromatic hydrocarbons, steroids, herbicides, etc. [3].

We formerly prepared a homologous series of mesogenic aldehydes, 4-(ω -hydroxyalkoxy)-4'-formylazobenzenes [4] whose significant feature was an enhanced thermal stability and extended temperature range of the mesophase. This effect of the terminal hydrophilic substituent originates from the existence of supra-molecular chain associates owing to the presence of sufficiently strong intermolecular hydrogen bonds.

In continuation of the investigation of the effect of the hydroxy group in the terminal aliphatic substituent on the mesomorphous properties of substances and in order to obtain heat-resistant liquid crystals with a wide range of mesophase existence we synthesized in the present study 4-[4-(ω -hydroxyalkoxy)phenyl]diazenylcinnamic acids and their 4-cyanophenyl esters.

Obtained phenyldiazenylcinnamic acids **Ia–Ie** are crystalline substances of orange color; they were many times recrystallized from acetic acid and ethanol (see the scheme).

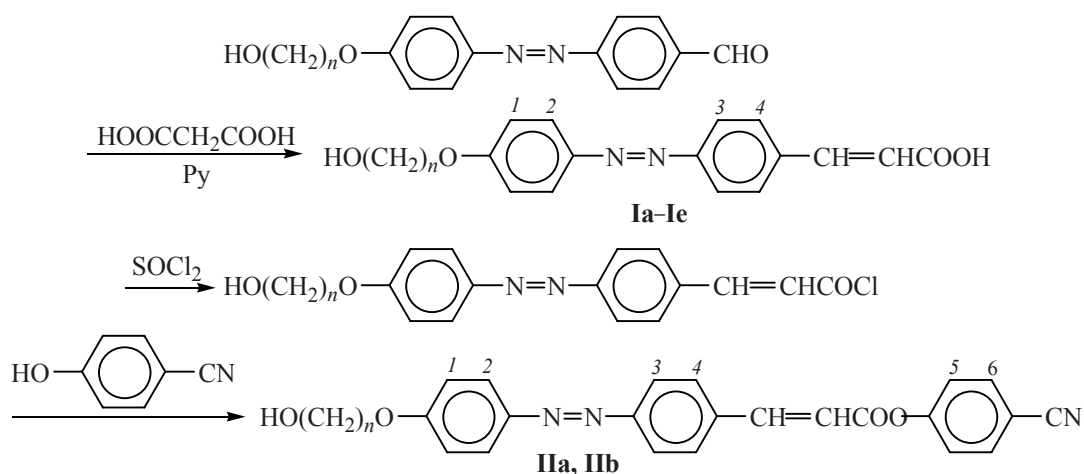
4-Cyanophenyl esters of 4-[4-(ω -hydroxyalkoxy)phenyl]diazenylcinnamic acids **IIa** and **IIb** are crystalline substances of orange-red color. They were purified by column chromatography on aluminum oxide (eluent chloroform) and recrystallized from ethanol.

The compounds synthesized were purified and kept in a vacuum till the constant temperature of their phase transitions and the absence in the ¹H NMR spectra of impurity signals.

The composition and structure of compounds obtained **Ia–Ie**, **IIa** and **IIb** were proved by elemental analysis (see the table), IR and ¹H NMR spectra. The parameters of the ¹H NMR spectra were fairly consistent with the characteristics calculated with the use of published data [5].

The temperature of phase transitions was measured by the method of polarization thermomicroscopy and is

Scheme.



$n = 2$ (a), 6 (b), 8 (c), 9 (d), 10 (e).

compiled in the table. Thermomicroscopy investigation of 4-[4-(ω -hydroxyalkoxy)phenyl]diazenyl cinnamic acids **Ia–Ie** showed that these compounds are high-melting, possess a considerable stability of the mesophase and a sufficiently wide range of its existence. Mesogenes **IIa** and **IIb** above their melting point are melts of low viscosity. In the polarized light schlieren-texture is observed in the melts characteristic of nematic mesophase.

Compound **Ia** does not exhibit the liquid crystal properties, evidently because the low geometrical anisotropy of the molecule, whereas the corresponding 4-cyanophenyl ester **IIa** is a liquid crystal. Compounds **IIa** and **IIb** with three aromatic rings have a significantly higher clearing points and a wider range of the mesophase existence than compounds **Ia–Ie** including two aromatic rings. This fact is understandable from the viewpoint of larger polarization anisotropy of compounds having three aromatic rings.

The comparison of the mesomorphic characteristics of obtained substances **Ia–Ie**, **IIa** and **IIb** with those of their structural analogs lacking the hydroxy group in the terminal substituent which we have synthesized and investigated earlier [6, 7] demonstrates a fairly significant effect of the terminal hydroxy group on the phase transition temperature. Therewith the active substituent to a greater extent increased the temperature of the nematic-isotrope transition than the melting point thus leading to a considerable extension of the temperature range of the nematic phase apparently because of the formation of sufficiently strong intermolecular associates bound by hydrogen bonds.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Avtar 360PT-IR ESP from pellets with KBr. ^1H NMR

Yield and characteristics of liquid crystalline acids $\text{HO}(\text{CH}_2)_n\text{OC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{CH}=\text{CHCOOH}$ **Ia–Ie** and their esters $\text{HO}(\text{CH}_2)_n\text{OC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{CH}=\text{CHCOOC}_6\text{H}_4\text{CN}$ **IIa, IIb**

Compound no.	Yield, %	Phase transition temperature, °C		Found, %			Formula	Calculated, %		
		C>N	N→I	C	H	N		C	H	N
Ia	68	–	240	65.28	5.24	8.92	$\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_4$	65.39	5.13	8.97
Ib	64	198	240	68.23	6.70	7.69	$\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_4$	68.48	6.52	7.61
Ic	69	190	235	69.76	7.12	7.42	$\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4$	69.7	7.07	7.07
Id	54	180	223	70.34	7.43	6.34	$\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$	70.24	7.32	6.23
Ie	63	187	220	70.63	7.62	6.52	$\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_4$	70.76	7.55	6.60
IIa	52	154	>300	67.58	4.79	10.98	$\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_4$	67.87	4.88	10.8
IIb	57	101	268	70.29	5.78	9.58	$\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_4$	70.43	5.64	9.48

spectra were registered on a spectrometer Bruker AC-200 at operating frequency 200.13 MHz from solutions in CDCl_3 , chemical shifts were measured relative to TMS with an accuracy no worse than ± 0.01 ppm.

The phase transition temperatures were measured and the textures of compounds obtained were examined on a polarization microscope Polam P211 equipped with a heating block. The errors in the measured phase transition temperatures were $\pm 0.2^\circ\text{C}$.

4-(ω -Hydroxyalkoxy)-4'-formylbenzenes were prepared by procedure [4]. 4-Hydroxybenzonnitrile for the synthesis of compounds **Ia** and **Ib** was obtained as described in [8].

4-[4-(2-Hydroxyethoxy)phenyl]diazenylcinnamic acid (Ia). A mixture of 2.7 g (10 mmol) of 4-(2-hydroxyethoxy)-4'-formylbenzene and 1.74 g (15 mmol) of malonic acid was boiled in 50 ml of anhydrous pyridine for 4 h. The reaction mixture was poured into ice water, the precipitate was filtered off, washed with water, and recrystallized from acetic acid and ethanol. Yield 2.12 g (68%). Orange crystalline substance, mp 240°C . IR spectrum, ν , cm^{-1} : 3405 (OH), 2945, 2860 (CH), 1693 (C=O). ^1H NMR spectrum, δ , ppm: 4.02 t (2H, HOCH_2), 4.13 t (2H, CH_2O), 7.07 d (2H, ArH^1), 7.93 d (2H, ArH^2), 8.00 s (4H, $\text{ArH}^{3,4}$), 11.37 s (1H, COOH).

Likewise were prepared compounds **Ib–Ie**.

4-Cyanophenyl 4-[4-(2-hydroxyethoxy)phenyl]diazenylcinnamate (IIa). A mixture of 3.12 g (10 mmol) of compound **Ia**, 2 ml of thionyl chloride, and 3 drops of pyridine were heated at 100°C for 2.5 h. Then in a vacuum the unreacted thionyl chloride was distilled off. The freshly obtained chloride of acid **Ia** was dissolved in 50 ml of ethyl ether and 1.19 g (10 mmol) of 4-hydroxybenzonnitrile in 70 ml of pyridine was added. The mixture was boiled for 3.5 h, the solution was poured into ice water acidified with HCl. The precipitate was extracted with chloroform, passed through a column packed with aluminum oxide (eluent chloroform), and recrystallized from ethanol. Yield

2.14 g (52%). Orange-red crystalline substance, mp 134°C . IR spectrum, ν , cm^{-1} : 2223 (CN), 3431 (OH), 2853, 2923 ($\text{CH}_{\text{aliphatic}}$), 1127–1734 (CH_{arom}). ^1H NMR spectrum, δ , ppm: 3.84 t (2H, HOCH_2), 4.31 t (2H, CH_2O), 5.1 s (1H, OH), 6.75 s, 6.55 d (1H, =CHOO), 7.93 d (1H, CH=), 7.03 d (2H, ArH^1), 7.31 d (2H, ArH^2), 7.70 d (2H, ArH^3), 7.74 d (2H, ArH^4), 7.82 d (2H, ArH^5), 7.91 d (2H, ArH^6).

Likewise was prepared compound **IIb**.

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