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# Mesogenic 4-(ω-Hydroxyalkoxy)-4'-formylazobenzenes

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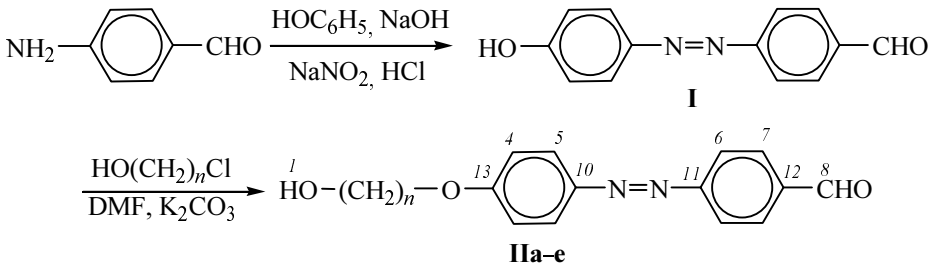
**Abstract**—Homologs from a series of 4-(ω-hydroxyalkoxy)-4'-formylbenzenes ($C_2$,$C_3$,$C_4$,$C_6$,$C_8$) were synthesized. All compounds obtained show properties of thermotropic nematic liquid crystals. The effect of the terminal hydroxy group of the end substituent on the mesomorphous properties of the compounds was analyzed.

Among the known liquid crystals [1] mesogenes with polar and chemically active substituents hold a special place. They attract interest due to ability to participate in strong specific selective interactions that considerably alter properties of mesophases, and thus these systems may be regarded as supramolecular liquid crystals [2]. Besides the presence of substituents like OH, COOH, CHO and others provides a possibility of further chemical modification of mesogenes aiming at extending the temperature range of mesophase existence, improving its thermal stability [3], imparting the liquid crystals special qualities, in particular, structural selectivity [4].

We formerly prepared a homologous series of 4-alkoxy-4'-formylbenzenes [5] possessing nematic and smectic mesomorphism. A curious feature of the liquid crystals obtained was the high packing density and uncommonly strong effect of aliphatic substituents length on the anisotropy of molecular polarizability of the mesogenic molecules [6].

In view of the above with the goal to investigate the effect of the terminal hydroxy group on the mesomorphous properties of mesogenic aldehydes we prepared 4-(ω-hydroxyalkoxy)-4'-formylbenzenes. The synthesis was carried out along the scheme:

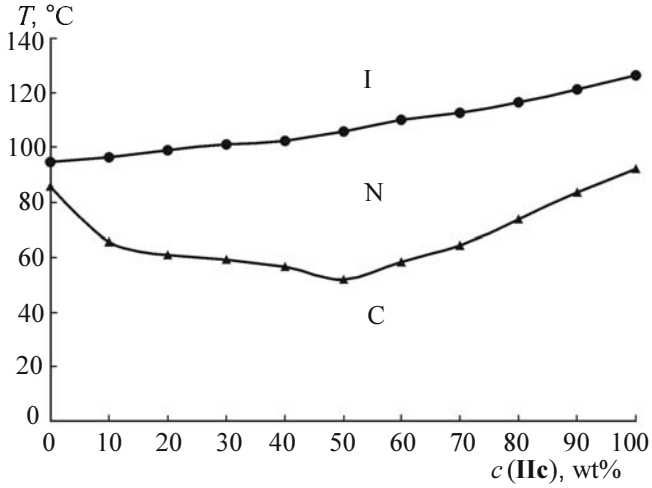



**II**, $n$ = 2 (**a**), 3 (**b**), 4 (**c**), 6 (**d**), 8 (**e**).

Azobenzenes **IIa–e** obtained (see table) are orange-red crystalline compounds that were recrystallized from ethanol and evacuated till constant temperature of phase transitions and lack of impurity peaks in their $^1$H NMR spectra.

The composition and structure of compounds **IIa–e** obtained were confirmed by elemental analysis (see table), IR, $^1$H and $^{13}$C NMR spectra. The experimental parameters of $^1$H and $^{13}$C NMR spectra are fairly consistent with the characteristics calculated along programs ACD-Labs.

Temperature of phase transitions of compounds synthesized was measured by the method of of polarization thermomicroscopy. The data obtained are




Phase diagram of binary mixture of 4-hydroxybutoxy-4'-formylbenzene (**IIc**) and 4-hexoxy-4'-formylbenzene (**IIId**) (I, N, C are isotropic, nematic, and crystalline phases respectively).

given in the table. The investigation demonstrated that all azobenzenes **IIa–e** behave as liquid crystals forming a nematic phase in sufficiently wide temperature range. The mesophases were identified by miscibility of compounds obtained with 4-hexoxy-4'-formylazobenzene (**IIId**) that exhibited nematic liquid crystal properties in the range 86–95°C [5]. The analysis of phase diagrams shows that the liquid crystals under study possess unlimited miscibility in the nematic region (see figure).

The comparison of the properties of compounds obtained with those of their analogs, 4-alkoxy-4'-formylazobenzenes [5], (see table) reveals a significant effect of the terminal hydroxy group on the phase transition temperature. Therewith the active substituent stronger increases the temperature of the transition from the nematic to isotropic state than the melting point thus considerably extending the temperature range of the nematic phase. This phenomenon apparently originates from the strengthening of cohesion interactions both in the crystal and in the mesophase, and in the latter as seen from its higher thermostability the additional intermolecular interactions are essentially anisotropic. Taking into account the weak orientational ordering of aliphatic substituents [7] and the orientation of the dipole moment of the hydroxy group the considerable contribution of dipole-dipole interactions with its participation may be excluded. In this case the effect of the hydroxy substituent may be produced solely by formation of sufficiently strong intermolecular hydrogen bonds. Inasmuch as hydroxy and aldehyde groups are complementary in the H-complexing, as one of arising supramolecular mesogenic structures may be anticipated a chain associate **A** built by the type "head-to-tail". However the interaction affording dimers **B** by the type "tail-to-tail"cannot be disregarded.

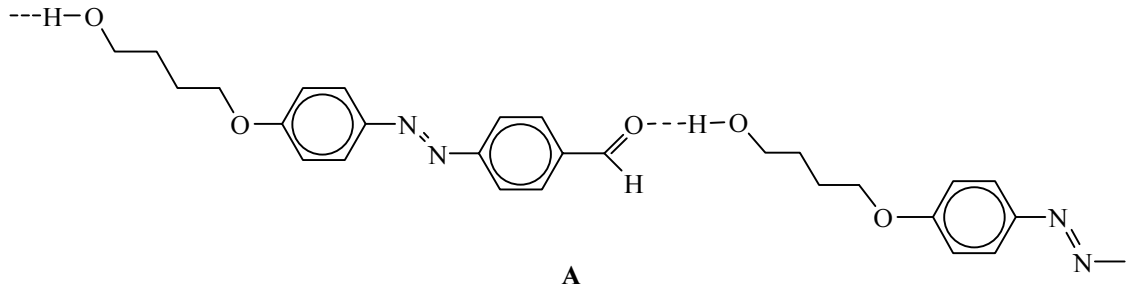
Both processes should increase the effective anisotropy of the molecular polarizability and consequently should result in increased mesophase thermostability. The disclosure of prevailing mechanism of the specific intermolecular interaction requires investigation of anisotropic physical characteristics of liquid crystals obtained and described in the present article.

## EXPERIMENTAL

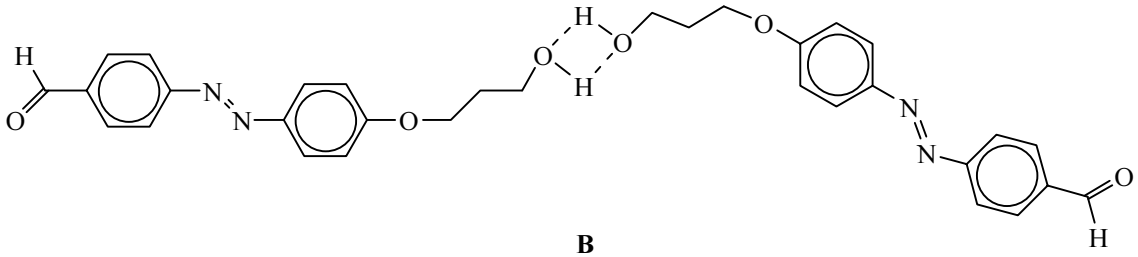
IR spectra were recorded on Avatar 360FT-IR ESP instrument from samples pelletized with KBr. NMR spectra were registered on spectrometer Bruker-AC200 at operating frequancies 200.13 ($^1$H) and 50.32 MHz

Yield and characteristics of mesogenic aldehydes $HO(CH_2)_nOC_6H_4N{=}NC_6H_4CHO$ (**IIa–e**)

| Compd. no. | Yield, % | Temperature of phase transitions, °C | | | | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **II** | | **III** [5] | | | | | | | | |
| | | C→N | N>I | C>N | N>I | C | H | N | | C | H | N |
| **IIa** | 92 | 125.3 | 146.7 | 114 | 118 | 67.31 | 5.84 | 9.87 | $C_{15}H_{14}N_2O_3$ | 66.67 | 5.19 | 10.37 |
| **IIb** | 90 | 96.4 | 146.0 | 83 | 97 | 68.25 | 6.04 | 10.15 | $C_{16}H_{16}N_2O_3$ | 67.61 | 5.63 | 9.86 |
| **IIc** | 88 | 92.1 | 126.3 | 94 | 99 | 69.34 | 6.70 | 8.80 | $C_{17}H_{18}N_2O_3$ | 68.46 | 6.04 | 9.40 |
| **IId** | 94 | 98.2 | 133.1 | 86 | 95 | 70.43 | 7.28 | 9.07 | $C_{19}H_{22}N_2O_3$ | 69.94 | 6.75 | 8.59 |
| **IIe** | 92 | 105.7 | 120.1 | 93 | 98 | 71.68 | 7.96 | 8.53 | $C_{21}H_{26}N_2O_3$ | 71.19 | 7.34 | 7.91 |



**A**



**B**

($^{13}$C). Chemical shifts were presented in δ-scale with respect to TMS and were measured from internal references TMS ($^1$H) and cyclohexane, 27.6 ppm ($^{13}$C–{$^1$H}). The error in recalculation of the chemical shifts in the $^{13}$C NMR spectra did not exceed ±0.01 ppm.

The phase transition temperature was measured and textures of compounds obtained were investigated with the use of polarization microscope Polam P-211 equipped with a heating block. The phase transition temperatures were measured with an accuracy ±0.2°C.

**4-Hydroxy-4'-formylazobenzene (I).** A suspension of 18.3 g (150 mmol) of 4-aminobenzaldehyde was prepared at 0°C in 100 ml of water. At the same temperature was separately dissolved 9.9 g (160 mmol) of sodium nitrite in 50 ml of water. To the suspension of 4-aminobenzaldehyde was simultaneously added at vigorous stirring the solution of sodium nitrite and 50 ml (330 mmol) of 24% hydrochloric acid solution maintaining the pH of the reaction mixture at 7. The completion of diazotization was checked by a starch-iodide paper strip test. The solution of diazo compound was adjusted to pH 7 by adding 4% NaOH solution. To the neutral solution of diazo compound at cooling and stirring was added a cooled to 0°C solution of 14.2 g (150 mmol) of phenol in 50 ml (150 mmol) of 6% NaOH solution. The end of the azo coupling was checked by a drop test with sodium phenolate. The reaction product was precipitated by adding to the reaction mixture 60 g of NaCl, the precipitate was filtered off, and recrystallized from 80% acetic acid. Yield of bright-orange crystalline compound **I** 29.9 g (87%), mp 185°C.

**4-(2-Hydroxyethoxy)-4'-formylazobenzene (IIa).** A mixture of 2.3 g (10 mmol) of compound **I**, 0.81 g (10 mmol) of ethylene chlorohydrin, and 1.66 g (12 mmol) of potassium carbonate in 150 ml of DMF was heated at reflux at vigorous stirring for 4 h. The hot reaction mixture was poured into 400 ml of ice water, the precipitate was filtered off and dried in air. Then it was passed through a column packed with $Al_2O_3$ (eluent chloroform) and recrystallized from ethanol. Yield of orange crystalline compound **IIa** 2.5 g (92%), mp 131.7°C. IR spectrum, ν, cm$^{-1}$: 3415 (OH), 2950, 2869 (CH), 1698 (C=O). $^1$H NMR spectrum, δ, ppm: 4.02 t (2H, $HOCH_2$), 4.16 t (2H, $CH_2O$), 7.07 d (2H, Ar–H$^4$), 7.93 d (2H, Ar–H$^5$), 8.00 s (4H, Ar–H$^{6,7}$), 10.08 s (1H, CH$^8$O). $^{13}$C NMR spectrum, δ, ppm: 61.25 ($HOCH_2$), 69.53 ($CH_2OAr$), 114.85 (C$^4$), 123.04 (C$^5$), 125.34 (C$^6$), 130.67 (C$^7$), 136.93 (C$^{12}$), 147.17 (C$^{10}$), 156.04 (C$^{11}$), 161.85 (C$^{13}$), 191.69 (C$^8$). Found, %: C 67.31; H 5.84; N 9.87. $C_{15}H_{14}N_2O_3$. Calculated, %: C 66.67; H 5.19; N 10.37.

Likewise were prepared compounds **IIb–e**.

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REFERENCES

1. Grebenkin, M.F. and Ivashchenko, A.V., *Zhidkokristallicheskie materialy* (Liquid Crystal Materials), Moscow: Khimiya, 1989, 289 p.
2. Paleos, C.M. and Tsiourvas, D., *Liq. Cryst*., 2001, vol. 28, p. 1127.
3. Burmistrov, V.A., Kareev, V.Yu., and Koifman, O.I., *Zh. Org. Khim*., 1988, vol. 24, p. 1742.
4. Burmistrov, V.A., Shcherbakova, O.A., Kareev, V.Yu., and Koifman, O.I., *Zh. Aanalit. Khim*., 1990, vol. 45, p. 1781.
5. Burmistrov, V.A., Kareev, V.Yu, Korzhenevskii, A.B., and Koifman, O.I., *Izv. Vuzov, Ser. Khim. i Khim. Tekhnol*., 1986, vol. 29, p. 34.
6. Aleksandriiskii, V.V., Lobanova, S.A., Moryganova, Yu.A., Burmistrov, V.A., and Koifman, O.I., *Izv. Vuzov, Ser. Khim. i Khim. Tekhnol.,* 1994, vol. 37, p. 90.
7. Forster, P. and Fung, B.M., *J. Chem. Soc., Faraday, Trans. II*, 1988, vol. 84, p. 1083.