ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 3, pp. 393–395. © Pleiades Publishing, Inc., 2006.
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Mesogenic 4-Alkoxy-2-hydroxy-4'-formylazobenzenes

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Received April 25, 2005

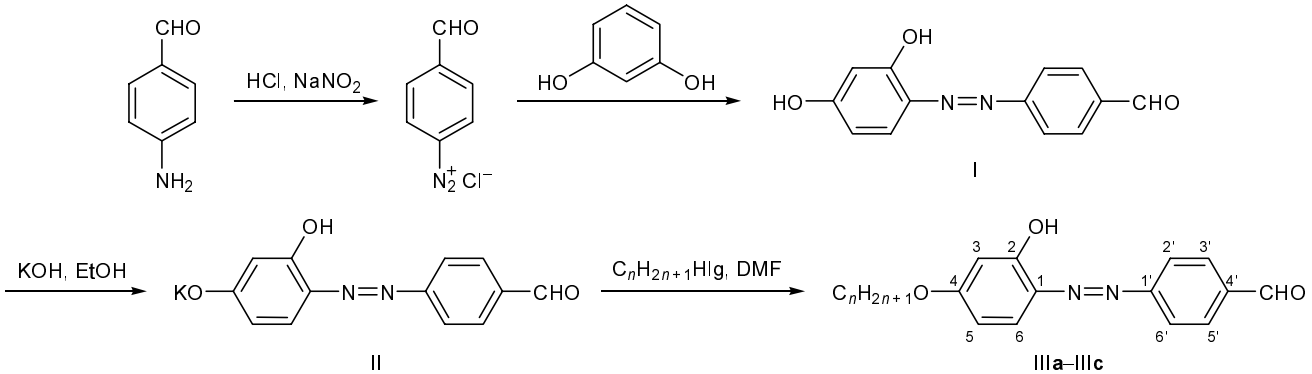
Abstract—Homologous 4-alkoxy-2-hydroxy-4'-formylazobenzenes (Alk = C_3H_7, C_6H_{11}, C_8H_{17}) were synthesized and were shown to produce monotropic nematic liquid crystalline phase. The products were characterized by electron absorption and ^1H and ^{13}C NMR spectra. The effect of lateral hydroxy group on their mesomorphic properties was analyzed.

DOI: 10.1134/S1070428006030092

Liquid crystalline state of a substance is characterized by a considerable fluidity and long-range orientation order which gives rise to anisotropy of physical properties. Therefore, mesogenic compounds are widely used in various fields of research, technics, and technology [1]. Further development of the synthetic potential of liquid crystals implies the use of unusual synthons (molecular fragments), including those containing chemically active terminal and lateral substituent groups. Interest in such compounds originates primarily from their ability for strong specific interactions which could affect their mesomorphic properties to a considerable extent, as well as from the possibility for their subsequent chemical modification [2].

We previously synthesized a series of homologous mesogenic aldehydes, 4-alkoxy-4'-formylazobenzenes, which revealed an anomalously strong effect of the length of the terminal alkoxy group on their anisotropic molecular polarizability [3]. In the present work we synthesized 4-alkoxy-2-hydroxy-4'-formylazobenzenes with a view to examine the effect of lateral hydroxy group on their mesomorphic properties. The synthesis was accomplished according to Scheme 1. The structure of newly synthesized compounds **IIIa**–**IIIc** was determined on the basis of the analytical and spectral data. The experimental ^1H and ^{13}C NMR parameters of compounds **IIIa**–**IIIc** were satisfactorily consistent with those calculated on the basis of published data [4]. The phase transition temperatures [crystalline→ nematic (Cr→N) and nematic→isotropic (N→I), °C], determined by polarization microscopy, are given below.

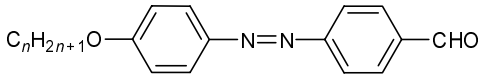
Scheme 1.



n = 3 (**a**), 6 (**b**), 8 (**c**).

Compound no.	**IIIa**	**IIIb**	**IIIc**
Cr→N	85.6	77.2	72.8
N→I	107.3	100.0	91.7

The results showed that all *ortho*-hydroxy-substituted formylazobenzenes **IIIa**–**IIIc** are nematic liquid crystals. Their structural analogs having no lateral hydroxy group, 4-alkoxy-4'-formylazobenzenes **IVa**–**IVc** [3], exhibit enantiotropic mesomorphism, and their nematic–isotropic transition temperatures regularly decrease as the length of the hydrocarbon chain in the alkoxy substituent increases. This is the result of loosening effect of aliphatic substituents, which also leads to extension of the mesophase temperature range.



IVa–IVc

n = 3 (**a**), 6 (**b**), 8 (**c**).

Introduction of a hydroxy group into the *ortho*-position with respect to the alkoxy group considerably affects mesomorphic properties of compounds **IIIa**–**IIIc** due to formation of strong intramolecular hydrogen bond. The thermal stability of mesophase is reduced, presumably owing to lateral extension of the mesogenic molecule as a result of formation of additional quasiaromatic H-chelate ring and the corresponding decrease of molecular polarizability.

Below are given the chemical shifts of the hydroxy and aldehyde protons in the ^{1}H NMR spectra of compound **IIIb** at different temperatures.

Temperature, °C	22	33	45
δ(OH), ppm	14.22	14.11	14.04
δ(CHO), ppm	10.02	10.02	10.02

It is seen that the OH signal shifts appreciably downfield as the temperature decreases. The reason is intramolecular hydrogen bonding between the hydroxy proton and nitrogen atom of the bridging N=N group. This is confirmed by the ^{13}C NMR spectra, as well as by published data [5]. Shielding of the hydroxy proton strongly depends on the temperature and properties of the medium. Rise in temperature should lead to rupture of intramolecular hydrogen bond and hence to upfield shift of the hydroxy proton (increased shielding), as illustrated by the above data. The position of the aldehyde proton signal does not change with temperature, indicating that this proton is not involved in intermolecular hydrogen bond.

The absorption maxima and molar absorption coefficients in the electron spectra of compounds **IIIb** and **IVb** are given below.

Compound no.	**IVb**	**IIIb**
λ_{max}, nm	369	401
A	0.48	0.60
log ε	4.38	4.48

Introduction of a hydroxy group into the aromatic chromophore produces a red shift and simultaneous broadening of the long-wave absorption band, as well as hyperchromic effect. This pattern is likely to result from both introduction of auxochrome and its participation in intramolecular hydrogen bond.

EXPERIMENTAL

The electron absorption spectra were measured on a UV/Vis Lambda 20 spectrophotometer from solutions in chloroform. The NMR spectra were recorded on a Bruker AC-200 spectrometer (200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C) using $CDCl_3$ as solvent; the proton chemical shifts were measured relative to tetramethylsilane, and the ^{13}C chemical shifts (^{13}C–{^{1}H}) were measured relative to cyclohexane (δ_C 27.6 ppm) and then recalculated to the δ scale with an accuracy of no less than ±0.01 ppm. A Polam P-211 polarizing microscope equipped with a temperature-control unit was used to determine the phase transition temperatures and examine the textures of the compounds under study. The error in the determination of phase transition temperatures was ±0.2°C.

4-(2,4-Dihydroxyphenyldiazenyl)benzaldehyde (I). 4-Aminobenzaldehyde, 18.3 g (150 mmol), was dispersed in 100 ml of water at 0°C. Sodium nitrite, 9.9 g (160 mmol), was dissolved separately in 50 ml of water at the same temperature. The resulting solution and 50 ml (330 mmol) of 24% hydrochloric acid were simultaneously added under vigorous stirring to the suspension of 4-aminobenzaldehyde, the mixture was adjusted to pH 7 by adding a 4% solution of sodium hydroxide, and a solution of 16.5 g (150 mmol) of resorcinol in 50 ml (150 mmol) of a 6% solution of sodium hydroxide, cooled to 0°C, was added to the neutral diazo component solution under stirring and

cooling. The product was filtered off, washed with water, and brought into further syntheses without recrystallization. Yield 24.8 g (68%), mp 200°C, dark red crystalline substance.

Potassium 4-(4-formylphenyldiazenyl)-3-hydroxybenzenolate (II). A mixture of 24.2 g (100 mmol) of compound **I** and 5.6 g (100 mmol) of potassium hydroxide in 150 ml of ethanol was heated for 3 h under reflux. The solvent was distilled off, and the residue was evacuated for 1 h at a residual pressure of 20 mm. Yield 26 g (93%), mp 215°C.

4-(4-Hexyloxy-2-hydroxyphenyldiazenyl)benzaldehyde (IIIb). A mixture of 2.8 g (10 mmol) of potassium salt **II** and 2.1 g (10 mmol) of hexyl iodide in 100 ml of DMF was heated for 4 h under reflux. The hot mixture was poured into ice water, and the precipitate was filtered off, washed with water, and dried in air. The product was applied to a column charged with Al_2O_3, the column was eluted with chloroform, the eluate was evaporated, and the residue was recrystallized from ethyl acetate. Yield 2.6 g (80%), mp 100°C, dark red crystalline substance. ^{1}H NMR spectrum, δ, ppm: 14.22 s (1H, OH), 0.90 t (3H, CH_3), 4.01 t (2H, OCH_2), 1.36 m (6H, CH_2), 1.80 t (2H, CH_2), 6.38 d (1H, 3-H), 6.61 d (1H, 5-H), 7.64 d (1H, 6-H), 7.95 m (2H, 5'-H, 6'-H), 10.03 s (1H, CHO). ^{13}C NMR spectrum, δ_C, ppm: 160.13 (COH), 14.01 (CH_3), 191.27 (CHO), 68.75 (CH_2O), 136.10 ($C^{4'}$), 130.96 ($C^{3'}$, $C^{5'}$), 121.31 ($C^{2'}$, $C^{6'}$), 152.97 (C^1), 135.19 (C^6), 110.78 (C^5), 101.77 (C^3). Found, %: C 70.00; H 6.72; N 8.55. $C_{19}H_{22}N_2O_3$. Calculated, %: C 69.94; H 6.75; N 8.59.

Compounds **IIIa** and **IIIc** were synthesized in a similar way.

4-(2-Hydroxy-4-propoxyphenyldiazenyl)benzaldehyde (IIIa). Yield 63%, mp 107.3°C. Found, %: C 67.54; H 6.02; N 10.17. $C_{16}H_{16}N_2O_3$. Calculated, %: C 67.61; H 5.63; N 9.86.

4-(2-Hydroxy-4-octyloxyphenyldiazenyl)benzaldehyde (IIIc). Yield 75%, mp 91.7°C. Found, %: C 72.52; H 7.20; N 7.90. $C_{21}H_{26}N_2O_3$. Calculated, %: C 71.19; H 7.34; N 7.91.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 05-03-32571a).

REFERENCES

1. Grebenkin, M.F. and Ivashchenko, A.V., *Zhidkocrystallicheskie materialy* (Liquid Crystalline Materials), Moscow: Khimiya, 1989.
2. Paleos, C.M. and Tsiourvas, D., *Liq. Cryst*., 2001, vol. 28, p. 1127.
3. Burmistrov, V.A., Kareev, V.Yu., Korzhenevskii, A.B., and Koifman, O.I., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol*., 1986, vol. 29, p. 34.
4. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Leningrad: Khimiya, 1983.
5. Fedorov, L.A., *Spektroskopiya YaMR organicheskikh analiticheskikh reagentov i ikh kompleksov s ionami metallov* (NMR Spectroscopy of Organic Analytic Reagents and Their Metal Complexes), Moscow: Nauka, 1987.