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HYDROXYL-CONTAINING MESOGENS. SYNTHESIS AND LIQUID-CRYSTALLINE PROPERTIES OF 2-*o*-HYDROXYARYLPYRIMIDINES

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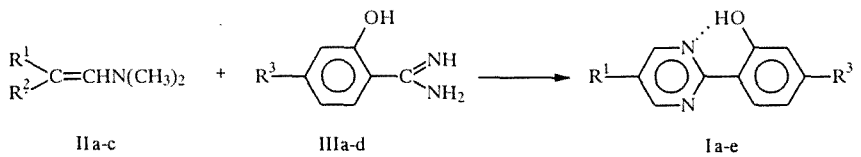
We have synthesized 5-alkyl(alkoxy)-2-(o-hydroxy-p-alkoxyphenyl)pyrimidines and considered the effect of the OH group on the mesomorphism. We have found that in binuclear o-*hydroxyarylpyrimidines, an* ortho *OH group forming an intramolecular hydrogen bond increases T_{mp}, inhibits the appearance of nematic properties, and promotes the appearance of a smectic A.*

Compounds forming a mesophase with participation of hydrogen bonds have many aspects with regard to the appearance of mesomorphism [1, 2], and in order to investigate the characteristics of the appearance of mesomorphism the search continues for new models for hydroxyl-containing mesogens [3-7].

For a new series of liquid-crystalline trinuclear 5-aryl-2-(*o*-hydroxyaryl)pyrimidines, it was shown earlier that compared with 2,5-diarylpyrimidines, the presence of an *ortho* OH group forming an intramolecular hydrogen bond leads to expansion of the range of the liquid-crystalline state, reduction of T_{mp}, and inhibition of nematic properties on a background of an increase in the tendency toward formation of a smectic phase, especially a smectic C with a broad temperature range [8].

In this paper, we have continued an investigation of the effect of the moiety forming the intramolecular hydrogen bond on the mesomorphism, for the example of binuclear *o*-hydroxyarylpyrimidines I. The group of alkyl, alkoxy-substituted 2-arylpyrimidines has been intensively investigated as low-melting, stable liquid crystals [9-12], widely used in various liquid-crystalline composites (for example, [13-15]). 5-Alkyl derivatives Ia-c were obtained by reaction of acroleins IIa,b with the corresponding *o*-hydroxyamidines III [8], and the 5-nonylhydroxypyrimidine Id was obtained by alkylation of 5-hydroxypyrimidine to Ie, synthesized according to the scheme developed in [16] from the corresponding 5-(dimethylaminomethylenamino)pyrimidine If.



IIa-c IIIa-d Ia-e

I, IIa $R^1 = C_6H_{13}$; I, IIb, Ic $R^1 = C_8H_{17}$; If, IIc R^1 = N=CHN$(CH_3)_2$; Id $R^1 = OC_9H_{19}$; Ie R^1 = OH; IIa,b R^2 = CHO; IIc R^2 = CH=N$(CH_3)_2$. ClO_4; I, IIIa $R^3 = OC_4H_9$; I, IIIb $R^3 = OC_8H_{17}$; I, IIIc R^3 = = H; Id–f, IIId $R^3 = OC_9H_{19}$

The *ortho*-hydroxyphenylpyrimidines Ia,b,d obtained displayed liquid-crystalline properties, considered in comparison with the properties of the corresponding *o*-alkoxy analogs: 5-hexyl-2-(p-butyloxyphenyl)- (40°C N 53°C I, IVa), 5-octyl-2-(p-octyloxyphenyl)- (28°C S_c 55°C S_A 62°C N 68°C I, IVb [9]), and 5-nonyloxy-2-(p-nonyloxyphenyl)- (65°C S_c 97°C S_A 101°C I, IVc [10]) pyrimidines. For all the hydroxyl-containing liquid crystals we observe an increase in T_{mp}, in the case of

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Ib reaching almost 30°C, and also an increase in the thermal stability of the mesophase for Ia,b; but on the whole, the range of the liquid-crystalline state is somewhat expanded only for Ia. With respect to this effect, the *o*-hydroxylaryl moiety in the binuclear hydroxyarylpyrimidines is different from its effect in trinuclear diaryl derivatives [8]. However, we also observe inhibition of the nematic properties (disappearance of the nematic mesophase in pyrimidines Ia,b compared with pyrimidines IVa,b) with predominance of the smectic. In contrast to trinuclear derivatives [8], compounds Ia,b are characterized by the appearance of only a smectic A, the thermal stability of which in the *o*-hydroxypyrimidine Ib is markedly higher than the corresponding stability in the analog IVb.

An attempt to affect the type of mesophase by introducing asymmetry in the substitution of the molecule was unsuccessful, since the structural prerequisites in compound Ic proved to be insufficient for the appearance of mesomorphism. Lengthening the alkyl chains of the substituent, used in dinoylhydroxypyrimidine Id, smoothes out the effect of the intramolecular hydrogen bond on the mesomorphic properties, and compound Id exhibits smectic mesomorphism in a similar temperature range, and only in a somewhat narrower interval than for the analog IVc not containing an intramolecular hydrogen bond.

EXPERIMENTAL

The temperature of the phase transitions, the types of mesophase, and the heats of the phase transitions for pyrimidine Ib were determined by thermal microscopy on a Boetius stage with an RNMK-05 visualization device and the Setaram DSC-111 scanning microcalorimeter. Symbols: S – smectic mesophase, N – nematic mesophase, I – isotropic melt.

The elemental analysis data for the compounds for C, H, N correspond to the calculated values.

5-Hexyl-2-(*o*-hydroxy-p-butyloxyphenyl)pyrimidine (Ia, $C_{20}H_{28}N_2O_2$). A solution of sodium methoxide, prepared from 0.46 g (20 millimoles) Na and 10 ml methanol, was added dropwise to a boiling suspension of 4.6 g (25 millimoles) acrolein IIa and 4.2 g (20 millimoles) benzamidine IIIa in 40 ml pyridine and then boiled for 10 h. The reaction mixture was cooled down to 20°C and added to 150 ml water, acidified with conc. HCl to pH 3. This was extracted (3 × 100 ml) with $CHCl_3$, dried, and the chloroform was driven off and the residue was passed through a column with AL_2O_3 in the system petroleum ether (40-60°C)–$CHCl_3$, 20:1, repeating the operation four times. The yield of pyrimidine Ia was 0.55 g (8%). The temperatures of the phase transitions were: 50.7°C S_A 71°C I. M^+ 328.2162.

5-Octyl-2-(*o*-hydroxy-p-octyloxyphenyl)pyrimidine (Ib, $C_{26}H_{40}N_2O_2$). A solution of sodium methoxide, prepared from 0.25 g (11 millimoles) Na and 15 ml methanol, was added to a boiling suspension of 3.59 g (17 millimoles) acrolein IIb and 3 g (11 millimoles) benzamidine in 60 ml alcohol with stirring, and then boiled for 20 h. The reaction mixture was cooled down to 20°C; the residue was filtered, washed with alcohol, and recrystallized three times from alcohol. The yield of pyrimidine Ib was 1.98 g (44%). Phase transition temperatures (ΔH° kcal/mole): 60.8°C (4.19) S_A 90.8°C (1.63) I.

5-Ocyl-2-(*o*-hydroxyphenyl)pyrimidine (Ic, $C_{18}H_{24}N_2O$). A solution of sodium methoxide, prepared from 0.12 g (5 millimoles) Na and 5 ml methanol, was added to a mixture of 1.27 g (6 millimoles) acrolein IIb and 0.68 g (5 millimoles) amidine IIIc in 10 ml alcohol, and then boiled for 20 h. The reaction mixture was evaporated; the residue was ground with 20 ml water, filtered, washed with water, and recrystallized three times from 40% alcohol. T_{mp} 35-36°C. Yield of pyrimidine Ic, 0.63 g (44%).

5-Nonyloxy-2-*o*-hydroxy-p-nonyloxyphenyl)pyrimidine (Id, $C_{28}H_{44}N_2O_3$). A mixture of 4.08 g (12 millimoles) hydroxypyrimidine Ie, 2.48 g (12 millimoles), nonyl bromide, 2.0 g (36 millimoles) KOH in 120 ml alcohol was boiled for 8 h. The residue was filtered and washed with chloroform, and the latter was combined with the alcoholic filtrate. The organic solvents were driven off and the residue was passed through a column with Al_2O_3; the eluent was petroleum ether, 70-100°C. The solvent was driven off and the residue was repeatedly passed through a column with Al_2O_3, first washing with hexane and then with a 5:1 hexane–ethylacetate mixture. Then the mixture was separated by TLC on silica gel in the system hexane–ethylacetate, 5:1, selecting the fraction with R_f 0.55. We obtained 0.13 g pyrimidine Id, forming a smectic mesophase with range 69-95°C. M^+ 456.3337.

5-Hydroxy-2-(*o*-hydroxy-p-nonyloxyphenyl)pyrimidine (Ie, $C_{19}H_{26}N_2O_3$). A mixture of 1 g (2.6 millimoles) pyrimidine If and 20 ml 2M H_2SO_4 was boiled for 1.5 h. The greenish residue was filtered; the impurity product 5-amino derivative was washed off with a 10% solution of $NHCO_3$, water, and acetone. Yield of pyrimidine Ie, 0.31 g (35%). T_{mp} 128-132°C. R_f 0.30 ($CHCl_3$ – alcohol, 20:1). M^+ 330.1961.

5-Dimethylaminomethylenamino-2-(*o*-hydroxy-p-nonyloxyphenyl)pyrimidine (If, $C_{22}H_{32}N_4O_2$). A solution of sodium methoxide, prepared from 0.35 g (15 millimoles) na and 10 ml methanol, was added dropwise to a boiling solution of 4.17 g (15 millimoles) amidine IIId and 4.45 g (15 millimoles) trimethinium salt IIc in 40 ml dry pyridine, and then boiled for 10 h. The reaction mixture was cooled down to 20°C, added to 200 ml water, acidified with conc. HCl. The residue was filtered, washed with water, and dried. The residue was recrystallized three times from alcohol and purified on a column with silica gel, chloroform as the eluent. The chloroform was driven off and the residue was recrystallize from methanol. T_{mp} 78-80°C. Yield of pyrimidine If, 2.37 g (41%). M^+ 384.2505.

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