5-ALKOXY-2-(*p*-CYANOPHENYL)PYRIMIDINES: NEW LOW-MELTING LIQUID CRYSTALS

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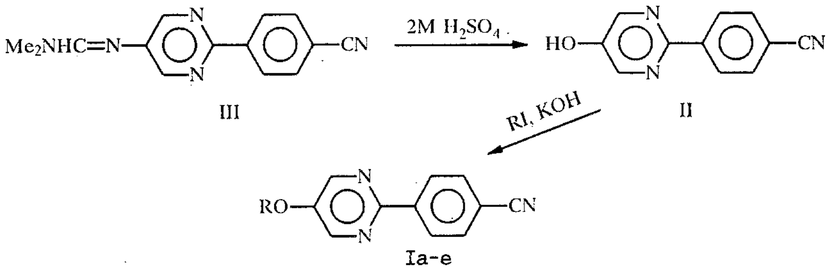
The C_4-C_8 homologues of new, stable, low-melting pyrimidine liquid crystals of the 5-alkoxy-2-(p-cyanophenyl)pyrimidine series have been synthesized. Their liquid-crystal properties have been studied, and it has been shown that the C_4-C_6 homologues manifest nematic properties, while the C_7 and C_8 homologues have a smectic mesophase along with the nematic mesophase.

Nematic liquid crystals, owing to their unique optical properties and low energy consumption, have found extensive use in information processing and display [1, 2]. In this area, *p*-cyano derivatives of the biphenyl, phenylpyridine, phenylpyrimidine, phenylcyclohexane, and other series are of practical importance [3]. Along with the lowest-melting and lowest-viscosity *p*-alkyl derivatives of these series, it is necessary in many cases to use the corresponding alkoxy derivatives [5] as mixture components, for example in the commercial mixtures Merck E3 and E8 [6]. An important step in improving the parameters of liquid-crystal indicator devices was taken when 5-alkyl-2-(*p*-cyanophenyl)pyrimidines were prepared and used — for example, materials of the ROTN-4 series [3, 7]. However, the corresponding alkoxypyrimidines (I), in contrast to the derivatives of other series, had not been reported up to the present time. Only the isomeric 5(2)-(*p*-alkoxyphenyl)-2(5)-cyanopyrimidines had been investigated; these compounds have melting points of 100°C or higher and tend to manifest smectic properties [7, 8].



Ia R = Bu; b R = C_5H_{11}; c R = C_6H_{13}; d R = C_7H_{15}; e R = C_8H_{17}

As described in the present article, we are proposing a method for obtaining 5-hydroxy-2-(*p*-cyanophenyl)pyrimidine (II), which is a predecessor in the synthesis of the pyrimidines (I). In this work, we obtained the C_4-C_8 derivatives Ia-e, studied their liquid-crystal properties, and compared them with the properties of the corresponding analogs in other series. When compound II was synthesized by traditional methods of introducing an OH group into position 5 of the pyrimidine ring, including stages of acid hydrolysis and hydrogenation [9], it became difficult to introduce the cyano group into the molecule. We solved this problem by the use of a method proposed in [10] for the synthesis of 5-hydroxypyrimidines by acid hydrolysis of 2-aryl-5-dimethylaminomethyleneaminopyrimidines. By heating the substituted pyrimidine III with 2 M sulfuric acid, we succeeded in obtaining the 5-hydroxypyrimidine II in good yield without affecting the cyano group. Then, by interaction of the hydroxy derivative II with alkyl halides, we obtained the alkoxy derivatives Ia-e; the characteristics of these compounds are listed in Table 1.

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TABLE 1. Characteristics of Pyrimidines I

Compound	Empirical formula	Phase transition temperatures, °C	R_f	Yield, %
Ia	$C_{15}H_{15}N_3O$	85 N 110 I	0,62	80
Ib	$C_{16}H_{17}N_3O$	74 N 85 I	0,50	85
Ic	$C_{17}H_{19}N_3O$	72 N 96 I	0,44	94
Id	$C_{18}H_{21}N_3O$	58 S 74 N 89 I	0,42	54
Ie	$C_{19}H_{23}N_3O$	72 S 92 N 99 I	0,40	60

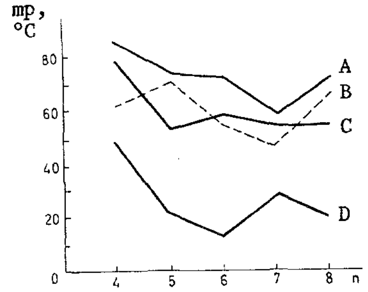

Fig. 1. Melting point of alkyl and alkoxy derivatives of *p*-cyanophenylpyrimidines and *p*-cyanobiphenyls as a function of length of aliphatic chain: A) 5-alkoxy-2-(*p*-cyanophenyl)pyrimidines; B) 5-alkyl-2-(*p*-cyanophenyl)pyrimidines; C) *p*-alkoxy-*p*′-cyanobiphenyls; D) *p*-alkyl-*p*′-cyanobiphenyls.

Liquid-Crystal Properties of Pyrimidines I

All of the synthesized pyrimidines Ia-e manifest liquid-crystal properties and can be characterized as stable, low-melting, enantiotropic liquid crystals. Even the C_4 homologue Ia has a good mesophase, in contrast to C_4 derivatives of other series that are either monotropic (biphenyls [11]) or are not liquid crystals (pyrazines [12, 13]). Compounds Ia-c manifest only nematic properties; the higher homologues Id,e form a smectic mesophase along with the nematic. The C_7 homologue Id has the widest interval of the liquid-crystal state, and also the lowest melting point. The three compounds Ib-d have relatively low temperatures of the transition to the nematic mesophase (72-74°C). The increase of melting point (Δmp) when the change is made from alkyl to alkoxy derivatives (for example, as much as 45° in the biphenyl series), on the one hand, or when the change is made from biphenyl to pyrimidine derivatives (as much as 40-50° for the alkyl series), on the other hand, proved to be less than expected in the case of the newly obtained cyanophenylpyrimidine derivatives I: The maximum increase of the melting point for the compounds Ia-e in comparison with the melting points of alkoxycyanobiphenyls and alkylcyanophenylpyrimidines was no more than 22°; this characterizes the compounds as low-melting liquid crystals (see Fig. 1).

EXPERIMENTAL

The individuality of compounds Ia-e was verified by TLC on Silufol UV-254 plates, in benzene. The phase transition temperatures and the mesophase types were determined on a small heated stage of the Boethius type with a PNMK-0.5 viewing device; the mesophases were classed as N (nematic), S (smectic), or I (isotropic).

Elemental analyses of compounds Ia-e, II, and III were in agreement with calculated values.

5-Dimethylaminomethyleneamino-2-(*p*-cyanophenyl)pyrimidine (III, $C_{14}H_{13}N_5$). This compound was prepared in accordance with [14] from 2-dimethylaminomethyleneamino-3-dimethylaminopropenylidenedimethylamine perchlorate [15] and *p*-cyanobenzamidine hydrochloride [16], with yields of 50-60%, mp 153-156°C (benzene).

5-Hydroxy-2-(*p*-cyanophenyl)pyrimidine (II, $C_{11}H_7N_3O$. To 10 ml of 2 M H_2SO_4, 1 g of the pyrimidine III was added, and the mixture was refluxed for 45 min. After cooling to 20°C, the precipitate was filtered off, washed with water (3 × 20 ml), and dried, obtaining the hydroxypyrimidine II with a yield of 0.75 g (99%), mp 235-236°C. R_f 0.40 (Silufol UV-254, $CHCl_3$–alcohol, 20:1). IR spectrum (KBr): 2230 cm^{-1} (CN).

5-Alkoxy-2-(*p*-cyanophenyl)pyrimidines Ia-e. First, 70 ml of DMF was added to 1 g (5 mmoles) of compound II; then, 5 mmoles of an alkyl iodide and 1.2 g of KOH were added, and the mixture was refluxed for 6-8 h. After cooling the reaction mixture to 20°, it was poured into 100 ml of water. The precipitate of I was either filtered out and washed with hexane, or it was recovered by extraction with $CHCl_3$, after which the extract was washed with water, dried over $MgSO_4$, and evaporated in a rotary evaporator. The pyrimidines Ia-e were purified as follows: Compound Ia was recrystallized three times from 40-70°C petroleum ether, chromatographed in a column with Al_2O_3 (hexane eluent, here and also for the other compounds), and again recrystallized from petroleum ether. Compound Ib was chromatographed twice in a column with Al_2O_3, each time recrystallizing the product from 40-70°C petroleum ether. Compound Ic was recrystallized twice from hexane, then chromatographed on Al_2O_3 and again recrystallized from hexane. Compound Id was recrystallized four times from 70-100°C petroleum ether, then chromatographed three times in a column with Al_2O_3 amd recrystallized from hexane. Compound Ie was chromatographed in a column with Al_2O_3 and then recrystallized from hexane.

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