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SYNTHESIS AND LIQUID CRYSTAL PROPERTIES OF ARYL ESTERS OF LATERALLY SUBSTITUTED 5-PYRIMIDINECARBOXYLIC ACIDS

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(p-R-phenyl)-4-methyl-, 4-methoxy-, and 4-hydroxy-5-pyrimidinecarboxylates have been synthesized and their liquid crystal properties examined. Compounds containing methyl and methoxy groups in the lateral position of the molecule are nematic liquid crystals with a mesophase range of 30-50°C, but the 4-hydroxy derivatives are smectic liquid crystals. With variants of the substituents in a series of (p-R-phenyl)-4-substituted 5-pyrimidinecarboxylates the mp of individual representatives were successfully reduced by ~50°C in comparison with the 4-unsubstituted analogs and the range of the mesomorphic state was extended to 190°C.

Keywords: arylcarboxylates, liquid crystals, lateral substituents, pyrimidines.

Mesomorphic derivatives of 2,5-disubstituted pyrimidines, containing an ester bridge in the structure are recommended as practically useful components of liquid crystal materials [1,2]. Among the compounds differing in structure by the mutual disposition of polar groups which influences the many parameters of the mesomorphic state, there are aryl esters of 2-substituted 5-pyrimidinecarboxylic acids, which are chiral smectic [3], antiferroelectrical [4], or nematic liquid crystals. For example as was shown in [5], aryl esters of 2-(*p*-R-phenyl)-5-pyrimidinecarboxylic acids are nematogens, in difference to the analogous compounds with a reversed disposition of the COO groups (i.e. obtained from 5-hydroxypyrimidines), characterized by the development of smectic properties [6].

On the other hand the influence of lateral substituents in rod-like liquid crystals on the mesomorphic state (the effect of a reduction of phase transition temperatures, the change of mesophase ranges and their thermostability, the predominance of nematics, etc.) with the aim of regulating the parameters of the liquid crystal state have been widely studied, and definite data have already been accumulated on the change of properties of a liquid crystal depending on the type and position of a substituent [7-9].

In the present work we have synthesized esters **1b-k** and have compared the overall influence of the side substituent R in the acid portion of the molecule and of the substituent R^1 of the phenolic fragment of esters **1b-k** on their liquid crystal properties with the unsubstituted analog **1a** which has a nematic phase in the range 124.8-195.8°C [5]. The initial esters **2a,c** were obtained by condensations known in pyrimidine chemistry of amidines with the appropriate ethoxymethylene derivatives of acetoacetic and malonic esters [5,10], and esters **2b,d** were obtained by conversions of the 4-hydroxy derivative **2c** [5].

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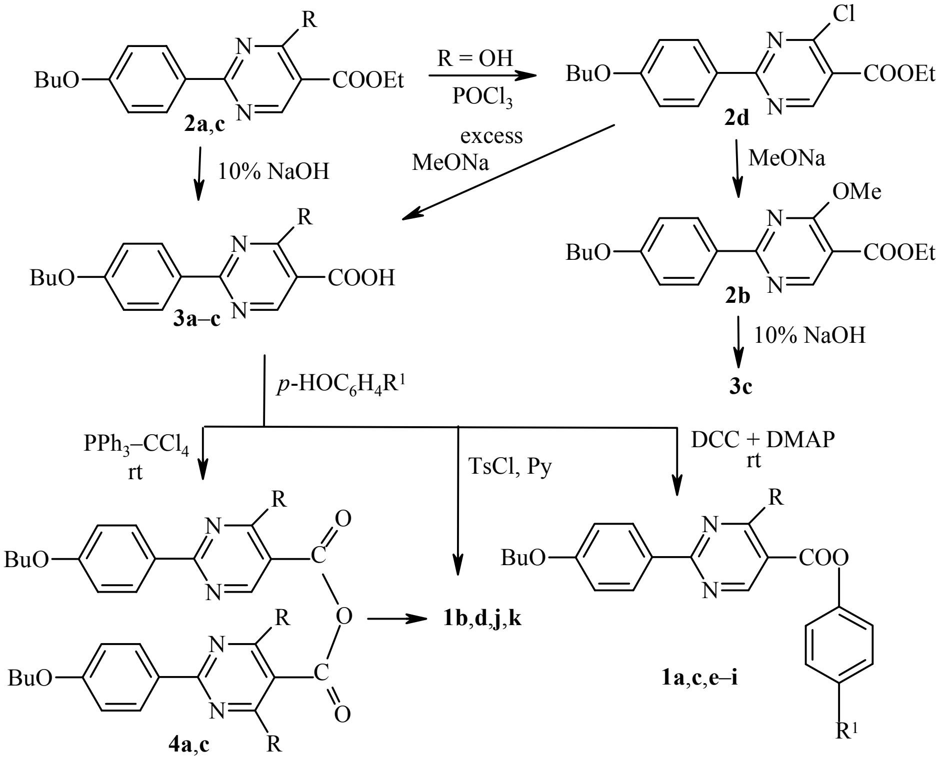
Scheme 1



1a R = H; **1b-f**, **2a-4a** R = Me; **1g-i**, **3b** R = OMe; **1j-k**, **2c-4c** R = OH*; **1 b**,**g**,**j** R^1 = Bu; **a**,**c**,**h** R^1 = Am; **d**,**i**,**k** R^1 = OBu; **e** R^1 = CN; **f** R^1 = COO-*p*-C_6H_4Am

Alkaline hydrolysis of the ethyl esters **2a,c** gave the corresponding acids **3a,c** but on hydrolysis of ester **2b** under the same standard conditions [5,10] ready fission of the methoxy group was observed and, in place of acid **3b**, the 4-hydroxy derivative **3c** was formed. The desired derivative **3b** was successfully obtained by treating the chloro derivative **2d** with an excess of sodium methylate. Under these conditions, contrarily, fission of the carbethoxy group was observed with retention of the methoxy group in the pyrimidine ring. It is interesting to note that in [11] the preparation of 4-methoxy-5-methoxycarbonyl-2-phenylpyrimidine was reported from the corresponding 4-chloro derivative by the action of an excess of sodium methylate.

For the synthesis of aryl esters **1** a method was selected using the PPh_3–CCl_4 complex at room temperature [12], previously well recommended when obtaining (aryl)pyrimidinyl-2-carboxylates [13]. However on interacting acid **3a** with *n*-butyl- or *n*-butyloxyphenol under the conditions in question the corresponding esters **1b,d** were not obtained. In the IR spectra of the reaction products an absorption band was observed for the C=O group of the initial acid (1690-1700 cm^{-1}), trace amounts of the desired esters (1730 cm^{-1}), and an absorption band at 1790 cm^{-1}, which we assigned to anhydride **4a**. Its formation was confirmed by mass spectrometric data on determining the molecular mass ($[M]^+$ 554). Analogously the interaction of hydroxy acid **3c** with *n*-butylphenol in the same system gave, according to data of IR and mass spectra, the same set of reaction products, namely the initial acid **3c** ($[M]^+$ 288, 1745 cm^{-1}), traces of ester **1j** ($[M]^+$ 420, 1714 cm^{-1}), and anhydride **4c** with $\nu_{C=O}$ 1773 cm^{-1}. For these cases we selected another method of obtaining aryl esters, the interaction of acids with phenols in the presence of *p*-toluenesulfonyl chloride at 90°C [14]. The use in this

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* Exist as the 4-oxo-3,4-dihydro derivatives.

reaction of both pure acids **1a,c** and of reaction mixtures from previous experiments enabled the synthesis in good yield of esters **1b,d,j,k**. Acid **3b** did not react under these conditions and was recovered in significant amounts from the reaction mixture. To obtain aryl esters of *o*-methoxy acid **3b** the carbodiimide method was used with dicyclohexylcarbodiimide (DCC) in the presence of 4-dimethylaminopyridine (DMAP) [5,15], which enabled the synthesis of aryl esters **1g-i**. Esters **1c,e,f** were synthesized under analogous conditions.

Investigation of the liquid crystal properties of the obtained esters showed that esters **1b-i** are nematic liquid crystals like analog **1a** described in the literature. Introduction of the 4-methyl group (esters **1b-d**) leads to a reduction in the phase transition temperature, which corresponds with the data of [8]. In comparison with

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			mp*, °C			IR spectrum, $\nu_{C=O}$, cm^{-1}	Yield, %
		C	H	N	N	I	S		
1b	$C_{26}H_{30}N_2O_3$	74.35 74.64	7.16 7.18	6.62 6.69	70	122		1740	50
1c	$C_{27}H_{32}N_2O_3$	74.98 75.00	7.62 7.40	6.42 6.48	77	129		1738	62
1d	$C_{26}H_{30}N_2O_4$	71.61 71.89	6.89 6.91	6.68 6.45	103	162		1717, 1737	46
1e	$C_{23}H_{21}N_3O_3$	70.87 71.32	5.36 5.43	10.72 10.85	138	194		1737 *[2]	72
1f	$C_{34}H_{36}N_2O_5$	74.21 73.91	6.63 6.52	4.90 5.07	105	295 (dec.)		1737	68
1g	$C_{26}H_{30}N_2O_4$	72.24 71.89	6.98 6.91	6.46 6.45	80	105		1724, 1751	62
1h	$C_{27}H_{32}N_2O_4$	72.20 72.32	7.14 7.14	6.17 6.25	74	113		1748	74
1i	$C_{26}H_{30}N_2O_5$	69.36 69.33	6.70 6.67	6.20 6.22	113	143		1745	83
1j	$C_{25}H_{28}N_2O_4$	71.45 71.42	6.76 6.66	6.55 6.66	259	270 (dec.)	216	1665, 1714	72
1k	$C_{25}H_{28}N_2O_5$	68.30 68.80	6.46 6.47	6.40 6.42	280	285 (dec.)	240	1667, 1715	67
2a	$C_{18}H_{22}N_2O_3$	68.62 68.79	6.73 7.01	8.84 8.92	101-102			1720	86
2b	$C_{18}H_{22}N_2O_4$	65.16 65.45	6.65 6.67	8.92 8.48	106-107			1727	87
2c	$C_{17}H_{20}N_2O_4$	64.07 64.55	6.21 6.33	8.75 8.86	225-226			1660, 1705	53 (69 [5])
2d	$C_{17}H_{19}ClN_2O_3$*[3]	60.61 60.98	5.64 5.68	8.28 8.37	88-88.5 (79 [5])			1714, 1732	62 (52 [5])
3a	$C_{16}H_{18}N_2O_3$	67.31 67.13	6.33 6.29	9.72 9.79	219-221			1674, 1698	90
3b	$C_{16}H_{18}N_2O_4$	63.62 63.57	5.98 5.96	9.28 9.27	213-214			1677, 1698	83
3c	$C_{15}H_{16}N_2O_4$	62.45 62.50	5.70 5.55	9.45 9.72	255-258			1636, 1753	94

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* For compounds **1b-k** the temperatures for phase transitions are given (S smectic, N nematic mesophases, I isotropic melt), for compounds **2a-d** and **3a-c** the mp are given. Solvents for crystallization were methanol (**1g,d**), acetonitrile (**1j,k**), alcohol–methyl cellosolve (**2c, 3a**), alcohol–ethyl acetate (**3b**), and alcohol (for the remaining compounds).

*[2] 2222 cm^{-1} (C≡N).

*[3] Cl, found, %: 10.40; calculated, %: 10.63.

the mp of ester **1a** the mp of esters **1b,c** was reduced by ~50-55°C, but Tc* was reduced by ~70°C caused by contraction of the mesophase range. A somewhat smaller reduction of both the phase transition temperature and the mesophase range was observed for the *p*-butoxyphenyl ester **1d**.

Introduction of the *p*-cyanophenyl group (ester **1e**) into the molecular structure did not lead to the prospect of broadening the range of the nematic state. A significant effect was successfully obtained by the introduction of a second ester bridge into the rigid framework of ester **1c**. Diester **1f** is characterized by a mp 27°C higher than ester **1c** and also a significantly more thermostable mesophase and correspondingly to its almost 4 times greater range.

The presence in aryl esters **1** of a side methoxy group larger in size than a CH_3 group and creating an additional dipole moment at an angle to the long axis of the molecule, leads to destabilization of the mesomorphous state. As a result compounds **1g-i** both due to higher mp and due to reduced thermostability of the mesophase have a narrower range of the nematic state by 12-29°C compared with analogs **1b-d**.

The introduction of lateral methyl and methoxy groups into the acid portion of esters **1b-e,g-i** therefore leads to a reduction in the phase-transition temperatures, and within each series closely similar mesophase ranges are observed. The size of the effect also depends on the character of the substituent in the *p*-position of the phenolic fragment of the ester.

Liquid crystal compounds containing a 4-oxo-3,4-dihydropyrimidine fragment in the molecule are inclined to strong lateral intermolecular interactions and are characterized by more ordered smectic states [16]. The derivatives of oxodihydropyrimidines obtained in the present work, esters **1j,k**, also belong to the high melting smectogens with a narrow nematic mesophase.

EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a Vector 22 spectrometer in KBr disks. Phase transition temperatures and mesophase textures were determined on a small-scale Boetius type hot stage with a RNMK 0.5 visual attachment. The characteristics of esters **1** and of the initial compounds **2** and **3** are given in Table 1. Molecular masses were determined mass spectrometrically on a Finnigan MAT 8200 instrument.

Aryl Esters of 4-Methyl- and 4-Hydroxy-2-(*p*-butoxyphenyl)-5-pyrimidinecarboxylic Acids (1b,d,j,k). *p*-Toluenesulfonyl chloride (1.9 g, 10 mmol) was added in portions with stirring at room temperature to a mixture of acid **3a** or **3c** (5 mmol) and *p*-butyl- or *p*-butyloxyphenol (5.3 mmol) in dry pyridine (20 ml) and the mixture stirred for 1 h. The reaction mixture was then heated at 90°C on a water bath for 2 h, and cooled to room temperature. The solid ester was filtered off, washed with acidified water, then with water to neutral reaction, dried, and recrystallized.

Aryl Esters of 4-Methyl- and 4-Methoxy-2-(*p*-butoxyphenyl)-5-pyrimidinecarboxylic Acids (1c,e-i). 4-Dimethylaminopyridine (0,2 g, 2 mmol) and then in portions dicyclohexylcarbodiimide (0.51 g, 2.5 mmol) were added at room temperature to a suspension of acid **3a** or **3b** (2 mmol) and the appropriate *p*-substituted phenol (3 mmol) in methylene chloride (10 ml). A solution formed after a short time, but then a solid began to precipitate. The suspension was stirred at room temperature for 8 h and left to stand overnight. The precipitate (~0.5 g) of dicyclohexylurea was filtered off, the filtrate evaporated to dryness, and the residue triturated with alcohol. The aryl ester was filtered off, washed with alcohol, dried and recrystallized to constant phase transition temperature.

2-(*n*-Butoxyphenyl)-4-methyl-5-pyrimidinecarboxylic Acid Ethyl Ester (2a). Ethoxymethyleneacetoacetic ester (18.6 g, 0.1 mol) and *p*-butyloxybenzamidine hydrochloride (22.8 g, 0.1 mol) were dissolved in absolute alcohol (200 ml) and a solution of metallic Na (2.75 g, 0.12 mol) in absolute alcohol (50 ml) was added

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* Tc is the clear point (N–I transition).

dropwise. The reaction mixture was boiled for 5 h and cooled to room temperature. The precipitated solid was filtered off, washed with water, dried, and compound **2a** (19 g) was obtained.

2-(*p*-Butoxyphenyl)-4-methoxy-5-pyrimidinecarboxylic Acid Ethyl Ester. (2b). Derivative **2d** (8 g, 24 mmol) was added to a solution of sodium methylate (1.35 g, 25 mmol) in methanol (30 ml) and the reaction mixture was boiled for 2 h. After cooling, the solid was filtered off, washed with methanol, dried, and ester **2b** (7.3 g) was obtained.

Ethyl Esters of 2-(*p*-Butoxyphenyl)-4-oxo-3,4-dihydro- (2c) and 2-(*p*-Butoxyphenyl)-4-chloro-5-pyrimidinecarboxylic Acids (2d) were obtained by the method of [5].

2-(*p*-Butoxyphenyl)-4-methyl-5-pyrimidinecarboxylic Acid (3a) was obtained by the hydrolysis of derivative **2a** on boiling in 10% NaOH solution with subsequent acidification of the reaction mixture by analogy with [10].

2-(*p*-Butoxyphenyl)-4-methoxy-5-pyrimidinecarboxylic Acid (3b). A solution of metallic Na (1.6 g, 35 mmol) in absolute methanol (120 ml) was added to chloro derivative **2d** (4.76 g, 14 mmol) and the mixture was boiled for 1.5 h. The reaction mixture was cooled, and the solid filtered off. It was triturated with water to a pasty state and the mass acidified with 20% HCl to pH 2-3. The mixture was stirred for 1 h, the solid was filtered off, washed with water, dried, and acid **3b** (3.5 g) was obtained.

2-(*p*-Butoxyphenyl)-4-oxo-3,4-dihydro-5-pyrimidinecarboxylic Acid (3c). A 10% solution (78 g) of NaOH and alcohol (8 ml) was added to ester **2c** (5.6 g, 17.7 mmol) and the mixture boiled for 2 h. The reaction mixture, which congealed on cooling, was filtered, the solid was triturated with water, and thoroughly washed several times with water and alcohol. After drying acid **3c** (4.8 g) was obtained.

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