2. Kh. Van Der Plas (H. C. Van der Plas), Khim. Geterotsikl. Soedin., No. 8, 1011 (1987).
3. D. J. Brown, The Pyrimidines, Interscience, New York–London (1962), p. 162.
4. N. B. Chapman and D. Q. Russel-Hill, J. Chem. Soc., No. 11, 1563 (1956).
5. K. Shirakawa, Yakugaku Zasshi, 79, 1477 (1959); Chem. Abstr., 54, 11038 (1960).
6. P. B. Terentiev, A. N. Kost, and J. Lange, J. Org. Mass Spectrom., 9, 1022 (1974).
7. J. D. Hennion and D. G. J. Kingston, Org. Mass Spectrom., 13, 431 (1978).
8. G. G. Danagulyan, N. G. Balasanyan, and M. G. Zalinyan, Khim. Geterotsikl. Soedin., No. 4, 563 (1988).
9. A. N. Kost, R. S. Sagitullin, and G. G. Danagulyan, Khim. Geterotsikl. Soedin., No. 5, 606 (1976).
10. A. N. Kost, R. S. Sagitullin, and G. G. Danagulyan, Khim. Geterotsikl. Soedin., No. 10, 1400 (1978).
11. H. C. Van der Plas and H. Yongejan, Rec. Trav. Chim., 89, 680 (1970).
12. F. Baumbach, H. G. Henning, and G. Hilgetag, Z. Chem., 4, 67 (1964).
13. D. J. Brown and J. A. Hoskins, J. Chem. Soc., Perkin I, No. 2, 522 (1972).

SYNTHESIS AND LIQUID CRYSTAL PROPERTIES OF SUBSTITUTED 1,4-BIS(PYRIMIDIN-2-YL)BENZENES

M. A. Mikhaleva, T. A. Kizner, N. I. Chernova, M. V. Loseva, G. A. Kolesnichenko, A. Z. Rabinovich, A. E. Kuznetsova, and V. P. Mamaev*

UDC 547.855.07:532.783

Some symmetrical and unsymmetrical alkyl-, alkoxy-, and acyloxy-1,4-bis(pyrimidin-2-yl)benzenes have been prepared, and their liquid-crystal properties examined. A distinguishing feature of these compounds is their ability to form only a nematic mesophase, the greatest range of liquid-crystal states and the lowest temperatures at which they appear being found in nonsymmetrical dialkoxy- and alkyl-alkoxy compounds.

The liquid-crystal properties of organic compounds are extremely sensitive to changes in the chemical structure of the molecule. There have been numerous publications in which changes in the aromatic ring system have been shown to not only reduce the lower limit of existence of the mesophase and increase thermal stability, and the criteria governing the type of mesophase established.

In this respect, the pyrimidine analogs of diphenyl and terphenyl systems are of considerable interest [1-3], and these have found practical application as components of liquid-crystal materials in various types of electrooptical equipment [4-6]. The pyrimidine analogs of diphenyl and terphenyl systems frequently enable the range of operating temperatures to be increased, the operating voltage to be reduced, and materials to be obtained having a lower viscosity-temperature relationship, which is of particular importance for equipment operating at temperatures below 0°C [7]. There have been recent reports of the synthesis and liquid-crystal properties of aryl derivatives of bipyrimidines of various types [8-11]. For example, some 1,4-bis(pyrimidin-2-yl)benzenes have been reported [11] to be liquid crystals of low viscosity with a wide range of mesophase, but only alkyl derivatives were considered, and only a single example was given, namely 5-pentyl-5'-propyl-1,4-bis(pyrimidin-2-yl)benzene, nematic liquid crystal in the temperature range 147-199°C.

*Deceased.

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Research Institute for Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1649-1657, December, 1989. Original article submitted July 8, 1988.

0009-3122/89/2512-1373$12.50

The present report describes the synthesis and liquid-crystal properties of the 1,4-bis-(pyrimidin-2-yl)benzenes (I-III), which are heterocyclic analogs of terphenyl containing two pyrimidine rings, in the search for liquid-crystal compounds with a nematic phase extending over a wide range and with high clarification temperatures (T_{cl}) for use as components for increasing the T_{cl} of liquid-crystal materials.

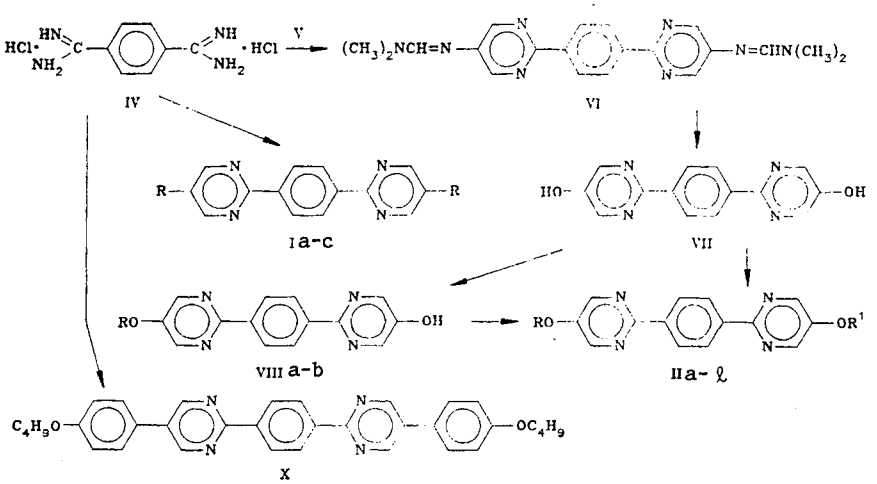
Synthesis of 1,4-Bis(pyrimidin-2-yl)benzenes (I-III). The previously unreported symmetrical alkylpyrimidinylbenzenes (Ia-c) were obtained by condensation of terephthalic acid diamidine (IV) with the appropriate alkyldimethylaminoacroleins. The oxygen-containing compounds (II) were obtained by first reacting the amidine (IV) with 2-dimethylaminomethyleneamino-3-dimethylaminopropenylidenemethylamine perchlorate (V) [12] to give 1,4-bis-(5-dimethylaminomethyleneaminopyrimidin-2-yl)benzene (VI), which on hydrolysis with sulfuric acid (2 mole/liter) [13] gave the dihydroxy-compound (VII) as a high-melting, sparingly soluble solid. The symmetrical dialkoxy-compounds (IIa-e) were obtained in high yields by boiling the dihydroxypyrimidine (VII) with the appropriate alkyl halides in ethyl cellosolve, in which the starting material (VII) is readily soluble, the disubstitution product separating as a solid. Alkylation of the dihydroxypyrimidine (VII) in alcoholic KOH proceeded much more slowly, and even after boiling for 45 h TLC and mass spectrometry showed the presence in the reaction mixture of the starting material and the monosubstitution product, which was difficult to separate from (II) (Scheme 1).

When the dihydroxypyrimidine (VII) was alkylated in DMF, advantage was taken of the differences in the solubilities of the mono- and dialkoxy-derivatives to obtain an adequately pure sample of the mono-alkoxy compound (VIIIa), required for the subsequant synthesis of unsymmetrical compounds. For example, alkylation of (VIIIa) with propyl bromide in DMF proceeded smoothly to give the propyloxypentyloxypyrimidine (IIf).

An examination of the acyloxy-compounds of (VII) was of independent interest, since esters form a very general and practically important group of liquid crystals, as exemplified by the esters of hydroquinone [14], 4,4'-dihydroxybiphenyl [15, 16], and other systems.

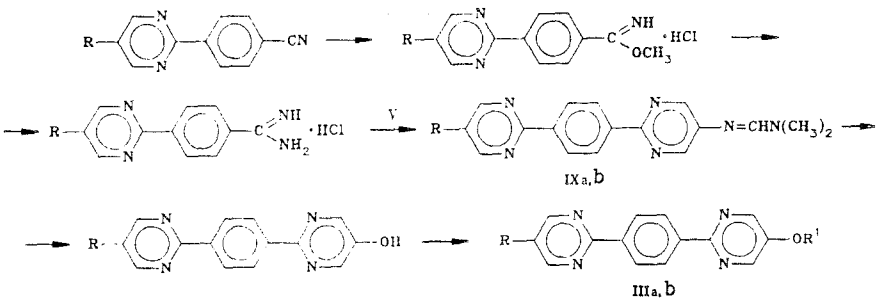
In order to examine their liquid-crystal properties, we prepared acyl derivatives of the dihydroxypyrimidine (VII) differing in the type and lengths of the terminal groups. The first member of the series was obtained by boiling (VII) in acetic anhydride to give the diacetyl compound (IIg). Acylation of (VII) with acid chlorides in the usual way [17] (pyridine, room temperature) was very slow, and difficultly separable mixtures of products were obtained. Under these conditions it was, however, possible to isolate a monoacylated product, the hydroxycaproyloxypyrimidine (VIIIb). When the reaction was carried out in a mixture of pyridine and monoglyme, higher yields of the diacylated pyrimidine (VII) were obtained, and this method was used to obtain the p-heptylbenzoyl (IIh) and butyryl (IIi) esters from the acid chlorides.

Scheme 1



Ia, IIa, f R=C_3H_7; IIa, i R^1=C_3H_7; IIb R, R^1=C_4H_9; Ib, IIi ℓ, VIIIa R=C_5H_{11}; IIc, f R^1=C_5H_{11}; Ic IId R, R^1=C_7H_{15}; IIe R, R^1=C_8H_{17}; IIg R, R^1=$COCH_3$; II R, R^1=$COC_6H_4C_7H_{15}$-*p*; II i R=COC_3H_7; IIi,m R^1=COC_3H_7; IIi R, R^1=$COC_6H_{10}C_4H_9$-*trans*; IIk R, R^1=$COC_6H_{10}C_6H_{13}$-*trans*; VIIIb R=COC_5H_{11}

Scheme 2



IIIa, IXa $R=C_3H_7$; IIIb $R=C_5H_{11}$; IIIa $R^1=C_5H_{11}$; IIIb $R^1=C_3H_7$

Acylation of the pyrimidine (VII) with 4-alkyl-trans-cyclohexane-1-carbonyl chlorides was carried out in pyridine over extended periods of time to give the diacyl derivatives (IIj) and (IIk).

The unsymmetrical alkoxyacyloxy-derivative (IIℓ) was obtained by acylating the alkoxy-hydroxypyrimidine (VIIIa) with butanoyl chloride in a mixture of pyridine and monoglyme.

Based on the method used by the authors to obtain 2-aryl-5-hydroxypyrimidines [13], we have devised a convenient route to oxygen-containing 1,4-bis-(pyrimidin-2-yl)benzenes, including unsymmetrical alkylalkoxy-compounds, since it is known [2] that asymmetry has a favorable effect on liquid-crystal properties. Taking advantage, therefore, of the simple methods of synthesis of 2-(p-cyanophenyl)-pyrimidines [18] and 5-hydroxypyrimidines [13], we have obtained the unsymmetrical alkylalkoxy-compounds (III) via the intermediates (IX), as shown in Scheme 2.

In addition, for comparison of their liquid-crystal properties, together with the three-ring systems (I-III), which are tetraaza-analogs of terphenyl, we have obtained a symmetrical five-ring analog of p-quinquephenyl [19], namely 1,4-bis-[5-(p-butyloxyphenyl)pyrimidin-2-yl]benzene (X).

Liquid-Crystal Properties of Substituted 1,4-Bis(pyrimidin-2-yl)benzenes (I-III). It is well known that in the great majority of cases compounds containing the terphenyl framework with various terminal substituents characteristically form the smectic phase A and more highly ordered orthogonal phases (smectic phases B and E) [20]. When the central benzene ring is replaced by the pyrimidine ring, there is a marked extension of the mesophase range (up to 100°C) [21], and a reduction in the phase-transition temperatures (especially the melting points). In the latter case, in addition to the inclined smectic C phase and the orthogonal smectic A phase characteristic of this group of compounds, there is also an injection of the nematic phase. It appears that increasing the numbers of ring nitrogen atoms in structurally analogous three-ring systems favors the ability of the compounds to display nematic properties, and this is also confirmed, for example, by the transformation of the smectogenic 2,5-diarylpyrimidines into the solely nematic 3,6-diaryltetrazines [22].

In all likelihood the observed differences in the liquid-crystal properties of 4,4'-terphenyls and 2,5-diarylpyrimidines is due to the more planar structure of the latter as a result of the decrease in the angle of twist between the pyrimidine and the 2-phenyl rings resulting from differences in the interactions between the hydrogen atoms in the ortho-positions in terphenyl, and between the ortho-H atoms and the lone electron pairs of the nitrogen atoms in 2-arylpyrimidines [23].

An effect of the geometrical structure of the molecule on liquid-crystal properties which is similar in type, but much more pronounced may be seen by comparing the properties of 2-aryl-5-alkyl- [24] and 5-aryl-2-alkylpyrimidines [22] with terminal substituents of the same length. In consequence of the reduction in the angle of twist to <10° between the phenyl and pyrimidine rings in the 2-phenylpyrimidines, as compared with angles of >20° in 5-phenylpyrimidines [25], only the nematic phase is present in 2-arylpyrimidines even with quite lengthy terminal substituents [24].

Accordingly, 1,4-bis(pyrimidin-2-yl)benzenes should have a structure with virtually planar (coplanar) geometry and, therefore, should display predominantly nematic properties. The data presented in Table 1 are in good agreement with these considerations. All the 1,4-bis(pyrimidin-2-yl)benzenes (I-III) [except for (IIh)] formed a nematic phase only.

TABLE 1. Properties of 1,4-Bis(pyrimidin-2-yl)benzenes

Compound	Empirical formula	T_n	T_{cl} (solvent for recrystallization)	ΔT, °C	Yield, %
Ia	$C_{20}H_{22}N_4$	185	213 (alcohol)	28	57
Ib	$C_{24}H_{30}N_4$	179,0*	189,5* (alcohol)	10,5	27
Ic	$C_{28}H_{38}N_4$	158,5*	178...181* (alcohol)	22,5	33
IIa	$C_{20}H_{22}N_4O_2$	202	252 (monoglyme)	50	77
IIb	$C_{22}H_{26}N_4O_2$	195	250 (monoglyme)	55	39
IIc	$C_{24}H_{30}N_4O_2$	200,5*	229,1* (monoglyme)	28,6	33
IId	$C_{28}H_{38}N_4O_2$	168,5*	213,0* (monoglyme)	44,5	94
IIe	$C_{30}H_{42}N_4O_2$	164,3*	207,9* (monoglyme)	43,6	82
IIf	$C_{22}H_{26}N_4O_2$	154	234 (alcohol)	80	99
IIg	$C_{18}H_{14}N_4O_4$	296**	313 (alcohol)	17	80
IIh	$C_{42}H_{46}N_4O_4$	222 (см)***	>360 (ethyl cellosolve)	>148	50
IIi	$C_{22}H_{22}N_4O_4$	245	300 (monoglyme)	55	23
IIj	$C_{36}H_{46}N_4O_4$	270	360 (ethyl cellosolve)	90	32
IIk	$C_{40}H_{54}N_4O_4$	245	345 (ethyl cellosolve)	100	33
IIℓ	$C_{23}H_{26}N_4O_3$	212	256 (monoglyme)	44	47
IIIa	$C_{22}H_{26}N_4O$	149,5*	213,6* (hexane)	64,1	57
IIIb	$C_{22}H_{26}N_4O$	155	206 (hexane)	51	30
VI	$C_{20}H_{22}N_8$	—	319...320 (ethyl cellosolve)	—	72
VII	$C_{14}H_{10}N_4O_2$	—	363...365	—	91
VIIIa	$C_{19}H_{20}N_4O_2$	—	>360 (monoglyme)	—	40
VIIIb	$C_{20}H_{20}N_4O_3$	—	332...334 (alcohol)	—	27
IXa	$C_{20}H_{22}N_8$	—	232...234 (alcohol-DMF)	—	63
X	$C_{34}H_{34}N_4O_2$	275 (см)	370 (monoglyme)	95	83

*Determined on a Mettler FP-52.
**Sublimed at 276°C.
***sm indicates smectic phase.

TABLE 2. Heats of Phase Transitions in 1,4-Bis(pyrimidin-2-yl)benzenes (Ib), (IIk), and (IIIa)

Compound	$T_c \rightarrow T_n$, °C	ΔH, kcal/mole	$T_n \rightarrow T_{cl}$, °C	ΔH, kcal/mole
Ib	176,5...179,5	6,48	186,5...187,8	0,34
IIk	255,7...260,7	4,51	340,5...343,0	0,55
IIIa	148,1...151,1	5,55	211,6...212,8	0,36

The symmetrical dialkyl compounds (Ia-c) have the smallest ranges of liquid-crystalline state, this range decreasing from the C_3- to the C_5-homolog. On passing from the alkyl compounds (I) to the symmetrical dialkoxy-derivatives (IIa-e), the range of the nematic mesophase is extended [to 50° and 30°C, respectively, for (IIa) and (IIc)], but the tendency to narrowing of the range from the C_3- to the C_5-homolog persists. The symmetrical compounds (IIg-k) have higher transition temperatures while retaining a wide mesophase range, with the exception of the first member of the series, (IIg). The high T_{cl} values of the acyl derivatives indicate the high thermodynamic stability of the mesophase.

Unsymmetrically 5,5'-substituted dipyrimidinyls show a tendency to extension of the mesophase temperature range, and a reduction in the temperature at which it appears, as compared with the corresponding symmetrical compounds. For example, in compounds (IIIa) and (IIIb) the temperature of transition to the nematic phase T_n is reduced by 30°C as compared with the dialkyl homologs (Ia) and (Ib), and by 50°C as compared with the dialkoxy-compounds (IIa) and (IIc). Similarly, in the alkoxyacyloxy-compound (III), T_n is reduced by 45°C as compared with the value for the pyrimidine (IIi). In the same compound (IIi), T_{cl} is increased as compared with the dipentyloxy-compound (IIc), and this is characteristic of acyl derivatives.

The most interesting properties were shown by the unsymmetrical compounds (IIf) and (IIIa, b), which had the lowest transition temperatures to the liquid-crystal state. Of these three compounds, the unsymmetrical dialkoxy-compound (IIf) had the greatest thermal stability, so that although the T_n values of these compounds were similar, the range of the liquid-crystal state in (IIf) was increased to 80°C.

The heats of the phase transitions to the nematic and isotropic state were measured for (Ib), (IIk), and (IIIa) (Table 2).

In contrast to the three-ring dipyrimidinylbenzene systems, the five-ring compound (X) had only a smectic mesophase over a wide temperature range and of high thermal stability, behavior which is characteristic of aromatic multiring compounds.

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer in KBr disks. PMR spectra were recorded on a Varian A56/60A spectrometer, internal standard HMS. Molecular masses were determined by mass spectrometry on a high-resolution Finnigan MAT-8200. Phase-transition temperatures and mesophase structures were determined on a Boetius micro-hot plate with an RNMK-0.5 visual attachment, and on a Mettler FP-52 polarizing microscope with a hot plate (indicated in Table 2 by an asterisk). The temperatures and heats of phase transitions were measured with a Setaram DSC-111 differential scanning calorimeter.

The elemental analyses of all the compounds [except for (VI)] corresponded to the calculated values. The elemental composition of (VI) was determined by high-resolution mass spectrometry.

1,4-Bis-(5-propylpyrimidin-2-yl)benzene (Ia). To a boiling suspension of 2.35 g (10 mmole) of the amidine (IV) and 2.85 g (20 mmole) of 2-propyl-3-dimethylaminoacrolein in 50 ml of absolute alcohol was added dropwise with stirring a solution of 1.62 g (30 mmole) of sodium methoxide in 15 ml of alcohol. The mixture was boiled for 13 h, the alcohol distilled off in a rotary evaporator, and the residue treated with 200 ml of water and filtered. The solid was washed with water and dried to give 1.8 g of the dipyrimidine (Ia). It was purified by repeated crystallization from alcohol with activated charcoal. PMR spectrum ($CDCl_3$): 0.9 (m, 3H, CH_3), 1.7 (m, 2H, C—CH_2—C), 2.6 (m, 2H, CH_2—C_{arom}), 8.6 and 8.7 ppm (s, 4H, H_{arom} and H_{pyrim}).

1,4-Bis-(5-pentylpyrimidin-2-yl)benzene (Ib). To a boiling suspension of 1.2 g (5 mmole) of the amidine (IV) and 1.69 g (10 mmole) of 2-pentyl-3-dimethylaminoacrolein in 50 ml of absolute alcohol was added with stirring a solution of 2.16 g (0.04 mole) of sodium methoxide in 15 ml of absolute alcohol. The mixture was boiled for 10 h, the alcohol distilled off, 100 ml of water added, and extracted with petroleum ether (3 × 30 ml). The petroleum ether was distilled off to give 0.54 g of the pyrimidine (Ib). The aqueous residue was extracted with chloroform, dried, and the chloroform removed to give a further 0.89 g of product. The overall yield of crude material was 1.43 g. Careful recrystallization from alcohol with activated charcoal gave 0.51 g of the pyrimidine (Ib).

Similarly, from the amidine (IV) and 2-heptyl-3-dimethylaminoacrolein there was obtained 1,4-bis-(5-heptylpyrimidin-2-yl)benzene (Ic).

1,4-Bis-(5-propoxypyrimidin-2-yl)benzene (IIa). A mixture of 2 g (7.5 mmole) of the dihydroxypyrimidine (VII), 3.1 g (25 mmole) of propyl bromide, 3 g (53 mmole) of KOH, 0.4 g of NaI, and 70 ml of ethyl cellosolve was boiled for 20 h, cooled, and the solid filtered off and washed with alcohol to give 2 g of the pyrimidine (IIa).

1,4-Bis(5-butoxypyrimidin-2-yl)benzene (IIb). A. A mixture of 2 g (7.5 mmole) of the dihydroxypyrimidine (VII), 3.43 g (25 mmole) of butyl bromide, 1.4 g of KOH, 0.3 g of NaI, and 60 ml of alcohol was boiled for 45 h, cooled, filtered from the solid (mp 219-228°C), the alcohol distilled off, and the residue treated with water. The solid was filtered off and washed with alcohol to give 1.93 g of product with a mesophase range 192-251°C.

B. A mixture of 1 g (3.8 mmole) of the dihydroxypyrimidine (VII), 1.7 g (12.5 mmole) of butyl bromide, 1 g of KOH, 0.2 g of NaI, and 60 ml of ethyl cellosolve was boiled for 7 h. The mixture was then cooled, and the solid filtered off and washed with alcohol to give 1.4 g of product with a mesophase range of 192-251°C.

The reaction products obtained by methods A and B were combined, washed carefully with alcohol, recrystallized from monoglyme, and purified on a column of silica gel in the system chloroform–acetone (8:1) to give 1.65 g of the pyrimidine (IIb).

1,4-Bis-(5-pentyloxypyrimidin-2-yl)benzene (IIc). A mixture of 2 g (7.5 mmole) of the dihydroxypyrimidine (VII), 4.8 g (25 mmole) of pentyl iodide, 3 g (53 mmole) of KOH, and 70 ml of ethyl cellosolve was boiled for 14 h, cooled, and the solid filtered off and washed with alcohol to give 1 g of the pyrimidine (IIc). PMR spectrum ($CDCl_3$): 0.90 (m, 3H, CH_3), 1.43-1.76 (m, 12H, C–CH_2–C), 4.10 (m, 4H, OCH_2), 8.46 ppm (s, 8H, H_{arom}).

1,4-Bis-(5-heptyloxypyrimidin-2-yl)benzene (IId) and 1,4-bis-(5-octyloxypyrimidin-2-yl)-benzene (IIe) were obtained similarly.

5-Pentyloxy-5'-propoxy-1,4-bis(pyrimidin-2-yl)benzene (IIf). To a mixture of 1 g (3 mmoles) of the pyrimidine (VIIIa) and 0.37 g (3 mmoles) of propyl bromide in 70 ml of DMF was added 0.6 g (10 mmoles) of KOH and 0.3 g of NaI, and the mixture stirred for 5 h at 70°C. The mixture was then filtered, the filtrate diluted with twice its volume of water, and the solid filtered off and washed with 15 ml of alcohol to give 1 g of the pyrimidine (IIf). PMR spectrum (acetone-D_6): 0.63-2.10 (m, 14H, CH_2–CH_3), 4.06 (t, 4H, OCH_2), 8.46 ppm (s, 8H, H_{arom}).

1,4-Bis-(5-acetoxypyrimidin-2-yl)benzene (IIg). A suspension of 0.35 g (1.3 mmole) of the hydroxypyrimidine (VII) in 20 ml of acetic anhydride was boiled for 2 h, cooled, and the solid filtered off and washed with water to give 0.37 g of the diacetoxy-compound (IIg). IR spectrum: 1770 cm^{-1} (C=O).

1,4-Bis-[5-(p-heptylbenzoyloxy)pyrimidin-2-yl]benzene (IIh). To a mixture of 2.66 g (10 mmoles) of the dihydroxypyrimidine (VII), 4.77 g (20 mmoles) of p-heptylbenzoyl chloride and 160 ml of monoglyme was added 20 ml of dry pyridine, and the mixture stirred at 20°C for 10 h. The solid was then filtered off and washed with ether (3 × 20 ml) and alcohol (2 × 20 ml) to give 3.42 g of the pyrimidine (IIh). IR spectrum: 1740 cm^{-1} (C=O).

1,4-Bis-(5-butanoyloxypyrimidin-2-yl)benzene (IIi). To a mixture of 1 g (3.8 mmoles) of the dihydroxypyrimidine (VII), 0.8 g (7.6 mmoles) of butyryl chloride and 70 ml of monoglyme was added 30 ml of dry pyridine, and the mixture stirred at 20°C for 30 h. It was then filtered, the filtrate poured onto 100 g of ice, and the resulting emulsion treated with petroleum ether (2 × 100 ml). The solid was filtered off, dissolved in chloroform, washed with acidified water (3 × 5 ml) to remove traces of pyridine, dried over $MgSO_4$, and evaporated. The residue was boiled with 20 ml of hexane and filtered to give 0.36 g of the pyridimidine (IIi). IR spectrum: 1760 cm^{-1} (C=O).

1,4-Bis-[5-(4-butyl-trans-cyclohexanoyl)pyrimidin-2-yl]benzene (IIj). A mixture of 1.55 g (7.5 mmoles) of 4-butyl-trans-cyclohexane-1-carbonyl chloride and 0.9 g (3.8 mmoles) of the dihydroxypyrimidine (VII) was stirred for 5 days at 20°C. The mixture was then poured into a mixture of 150 ml of concentrated HCl and 150 g of ice, stirred, and the solid filtered off, washed with water, and dried to give 2.4 g of crude product, which on purification gave 0.7 g of the ester (IIj).

1,4-Bis-[5-(4-hexyl-trans-cyclohexanoyl)pyrimidin-2-yl]benzene (IIk) was obtained similarly.

5-Pentyloxy-5'-butanoyloxy-1,4-bis(pyrimidin-2-yl)benzene (IIℓ). To 1 g (3 mmoles) of the pyrimidine (VIIIa) and 0.3 g (3 mmoles) of butyryl chloride in 40 ml of monoglyme was added 10 ml of dry pyridine, and the mixture stirred at 22°C for 20 h. The mixture was then filtered, the filtrate poured onto ice (50 g), and the resulting emulsion treated with petroleum ether (3 × 60 ml). The solid was filtered off, washed with acidified water

(3 × 5 ml), and dissolved in 40 ml of acetone. The acetone solution was filtered and evaporated to give 0.57 g of the pyrimidine (IIℓ), which was purified on a column of silica gel, eluent hexane. R_f 0.70 (Silufol UV-254, chloroform–alcohol, 10:1). IR spectrum, 1780 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 0.76-2.03 (m, 14H, CH_2CH_3 and $CH_2CH_2CH_2CH_3$), 2.57 (t, 2H, CH_2CO), 4.10 (t, 2H, CH_2O), 8.45 (s, 6H, H_{arom} + $H_{4,6}$-pyrim), 8.77 (s, 2H, $H_{4',6'}$-pyrim).

5-Propyl-5'-pentyloxy-1,4-bis(pyrimidin-2-yl)benzene (IIIa). A mixture of 2 g (5.8 mmoles) of the pyrimidine (IXa) and 3 ml of concentrated sulfuric acid in 30 ml of water was boiled for 3 h. After 30 min, the starting material had dissolved and another solid had begun to separate. The mixture was cooled and the solid filtered off, washed with water, and dried to give 1.3 g of 5-propyl-5'-hydroxy-1,4-bis(pyrimidin-2-yl)benzene. This hydroxy-compound (1.2 g, 4 mmoles) was mixed with 1.4 g (7 mmoles) of pentyl iodide and 1.12 g of KOH in 40 ml of ethyl cellosolve, and the mixture boiled for 10 h. It was then cooled and the solid filtered off and washed with hexane to give 0.8 g of the pyrimidine (IIIa). PMR spectrum ($CDCl_3$): 0.9 (t, 6H, CH_3), 1.10-1.70 (m, 8H, CH_2), 2.6 (t, 2H, C_5–CH_2), 4.07 (t, 2H, OCH_2), 8.47 (m, 6H, H_{arom} + $H_{4,6}$-pyrim), 8.6 ppm (s, 2H, $H_{4',6'}$-pyrim).

5-Pentyl-5'-propoxy-1,4-bis(pyrimidin-2-yl)benzene (IIIb). Into a solution of 5.1 g (20 mmoles) of 5-pentyl-2-(p-cyanophenyl)pyrimidine [18] in a mixture of 50 ml of benzene and 25 ml of methanol was passed dry HCl with cooling at 0°C until it was saturated (~45 min). The mixture was kept for 24 h at 20°C, evaporated to dryness in a rotary evaporator, the residue triturated with 75 ml of dry ether, and the solid filtered off and washed with dry ether (3 × 50 ml) to give 3.8 g (59%) of 5-pentyl-2-(p-carboxyphenyl)pyrimidine imino-ether hydrochloride, mp 228-230°C (from alcohol). PMR spectrum (DMSO-D_6): 0.33-1.93 [m, 11H, $(CH_2)_4$–CH_3], 2.6 (m, 3H, OCH_3), 3.2 (s, 1H, NH), 8.28 (q, 4H, H_{arom}), 8.90 ppm ($H_{4,6}$-pyrim). This hydrochloride was treated with 100 ml of chloroform and 100 ml of 20% NaOH, the mixture stirred for 10 min, the chloroform separated, and the aqueous layer extracted with chloroform (2 × 50 ml). The combined chloroform extracts were dried over $MgSO_4$, and the chloroform distilled off. The iminoether base was dissolved in 80 ml of alcohol, and 0.9 g of ammonium chloride added. This mixture was boiled for 2 h, evaporated, and to the residue was added 100 ml of dry ether. The solid was filtered off and washed with ether (4 × 30 ml) to give 3 g (90%) of 5-pentyl-2-(p-carboxyphenyl)pyrimidine amidine hydrochloride, mp 239-241°C (from alcohol). A mixture of 1.6 g (5 mmoles) of this amidine and 1.8 g (6 mmoles) of the salt (V) in 50 ml of methanol was brought to the boil, and a solution of 0.3 g (12 mmole) of sodium in 15 ml of methanol added dropwise with stirring. The mixture was boiled for 5 h, evaporated, 50 ml of water added, extracted with chloroform (3 × 30 ml), and the extracts dried over $MgSO_4$ and the chloroform removed to give 1.1 g (56%) of the pyrimidine (IXb). IR spectrum: 1420, 1640 cm^{-1}, mp 187-191°C. This pyrimidine (IXb) was boiled with 30 ml of 2 M sulfuric acid for 3 h, cooled to 20°C, and the solid filtered off and washed with water to give 0.3 g (28%) of 5-pentyl-5'-hydroxy-1,4-bis(pyrimidin-2-yl)benzene. This was mixed with 0.25 g (2 mmoles) of propyl bromide in 30 ml of ethyl cellosolve, and the mixture boiled for 10 h, filtered, diluted with 30 ml of water, and the pyrimidine (IIIb) (0.1 g) filtered off.

1,4-Bis-(5-dimethylaminomethyleneaminopyrimidin-2-yl)benzene (VI). To a boiling suspension of 86 g (0.29 mole) of the salt (V) and 33.3 g (0.14 mole) of terephthalic acid diamidine dihydrochloride in 300 ml of methanol was added dropwise a solution of 9.9 g (0.43 mole) of sodium in 500 ml of methanol. The mixture was boiled for 10 h, cooled, and the solid filtered off, washed with water and methanol, and dried to give 37.8 g of the dipyrimidine (VI). IR spectrum: 1100, 1270, 1400, 1570, 1640 cm^{-1}. R_f 0.3 (Silufol UV-254 in the system chloroform–alcohol, 20:1). Found: M^+ 374.1945. Calculated M 374.1967.

1,4-Bis-(5-hydroxypyrimidin-2-yl)benzene (VII). A suspension of 1 g (2.7 mmoles) of the dipyrimidine (VI) in 20 ml of 2 M sulfuric acid was boiled for 3 h, cooled, and the solid filtered off and dried to give 0.63 g (91%) of the dihydroxypyrimidine (VII), mp 363-365°C. IR spectrum: 1290, 1430, 1580 cm^{-1}. PMR spectrum (DMSO-D_6): 8.33 and 8.44 ppm (s, ratio of intensities 1:1, H_{arom} and H_{pyrim}).

5-Pentyloxy-5'-hydroxy-1,4-bis(pyrimidin-2-yl)benzene (VIIIa). To a mixture of 2 g (7.5 mmoles) of the dihydroxypyrimidine (VII) and 2.4 g (12 mmoles) of pentyl iodide in 35 ml of DMF was added 0.6 g (10 mmoles) of KOH, and the mixture stirred for 1 h at room temperature. The progress of the reaction was followed by TLC on Silufol in the system ethyl acetate–hexane (1:5). The mixture was heated to 70°C for 40 min. A clear, deep-green solution was first formed, which rapidly changed to a red-brown suspension. The mixture was

filtered [giving the dipentyloxy-compound (IIc), 0.6 g], and the filtrated diluted with one and a half volumes of water and the solid filtered off to give 1 g of the pyrimidine (VIIIa), R_f 0.9 (chloroform–alcohol, 10:1). IR spectrum: 1280, 1430 cm^{-1}. Found: M^+ 336.1582. $C_{19}H_{20}N_4O_2$. Calculated: M 336.1586.

5-Caproyloxy-5'-hydroxy-1,4-bis(pyrimidin-2-yl)benzene (VIIIb). To a mixture of 2.66 g (10 mmoles) of the dihydroxypyrimidine (VII) and 2.7 g (20 mmoles) of caproyl chloride was added 100 ml of dry pyridine, and the mixture stirred for 15 h at room temperature. It was then poured onto a mixture of 100 ml of concentrated hydrochloric acid and 100 g of ice, and the solid filtered off and dried. To this solid (1.43 g) was added 20-30 ml of acetone, 0.5 g of starting material (VII) filtered off, and the acetone filtrate evaporated to give 0.9 g of the pyrimidine (VIIIb), R_f 0.71 (chloroform–alcohol, 10:1). IR spectrum: 1060, 1430, 1760, 2880-2980, 3620 cm^{-1}. PMR spectrum (acetone-D_6): 0.8-2.8 (m, 11H, CH_2 and CH_3), 8.53 (s, 6H, H_{arom} + $H_{4',6'\text{-pyrim}}$), 8.77 ppm (s, 2H, $H_{4,6\text{-pyrim}}$).

5-Propyl-2-(p-cyanophenyl)pyrimidine. To a boiling suspension of 23.6 g (0.13 mole) of p-cyanobenzamidine hydrochloride and 20.1 g (0.143 mole) of 2-propyl-3-dimethylaminoacrolein in 250 ml of absolute alcohol was added dropwise with stirring a solution of 10.8 g (0.2 mole) of sodium methoxide in 60 ml of absolute alcohol. The mixture was boiled for 8 h, the alcohol distilled off, the residue treated with 0.5 liter of water, and the flocculent solid filtered off, washed with water, dried, boiled with 150 ml of pentane, cooled, and filtered to give 12.3 g of solid, mp 112-120°C. Recrystallization from alcohol with the addition of activated charcoal gave 8 g (28%) of product, mp 123.5-124.5°C. IR spectrum: 2220 cm^{-1}. Found: M^+ 223.1105. $C_{14}H_{13}N_3$. Calculated: 223.1109.

5-Propyl-5'-dimethylaminomethyleneamino-1,4-bis(pyrimidin-2-yl)benzene (IXa). A solution of 5 g (21.5 mmoles) of 5-propyl-2-(p-cyanophenyl)pyrimidine in 30 ml of dry dioxane and 15 ml of dry methanol was saturated with cooling with gaseous HCl (gain in weight of the reaction mixture, 28 g). After keeping at room temperature for 5 h, the mixture was evaporated, dry ether added, triturated, and 6.6 g of the iminoether hydrochloride, mp 235-240°C, filtered off. This was suspended in 45 ml of alcohol, gaseous ammonia passed in with cooling until saturated, and boiled for 4 h. The solid was filtered off and washed with ether to give 2.7 g of 5-propyl-2-(p-carbamoylphenyl)pyrimidine, mp 255-257°C (from alcohol). $C_{14}H_{15}N_3O$. After evaporation and washing with ether, from the filtrate there was obtained 2.8 g of 5-propyl-2-(p-amidinophenyl)pyrimidine hydrochloride, mp 240-255°C. To this was added a solution of 0.5 g of sodium in 50 ml of methanol and 3.7 g (0.015 mole) of the salt (V), and the mixture stirred for 1 h at room temperature, then boiled for 4 h. The solid which separated on cooling was filtered off to give 2.2 g of the pyrimidine (IXa).

1,4-Bis-[5-(p-butoxyphenyl)pyrimidin-2-yl]benzene (X). To a boiling mixture of 0.35 g (1.5 mmoles) of terephthalic acid diamidine dihydrochloride and 1.12 g (3 mmoles) of 2-(p-butoxyphenyl)-3-dimethylaminopropylidenedimethylamine perchlorate in 10 ml of absolute alcohol was added dropwise a solution of 0.16 g of sodium in 5 ml of alcohol, and the mixture boiled for 3 h. The solid was then filtered off and washed with water and alcohol to give 0.66 g of the pyrimidine (X), R_f 0.8 (Silufol UV-254, chloroform–alcohol, 20:1).

LITERATURE CITED

1. M. A. Osman, Mol. Cryst. Liq. Cryst., 128, 45 (1985).
2. A. Biering, D. Demus, L. Richta, H. Sackmann, A. Wiegeleben, and H. Zaschke, Mol. Cryst. Liq. Cryst., 62, 1 (1980).
3. H. Suenaga, S. Maeda, T. Iijima, and S. Kobayashi, Mol. Cryst. Liq. Cryst., 144, 191 (1987).
4. Kokai Tokkyo Koho 61-215373 JP; H. Suenaga, M. Taguchi, and T. Harada, Chem. Abstr., 106, 205,380 (1987).
5. M. Schadt, R. Buchecker, F. Leenhouts, A. Boller, A. Villiger, and M. Petrzilka, Mol. Cryst. Liq. Cryst., 139, 1 (1986).
6. K. Bofinger, R. Eidenschink, R. Hittich, R. Hopf, J. Krause, A. Pausch, V. Reiffenrath, B. Scheuble, and A. Waechter, GErm. Offen. 3518734 DE.
7. M. F. Grebenkii and V. A. Kozunov, Élektr. Prom., Nos. 5-6 (111-112), 20 (1982).
8. Kokai Tokkyo Koho 60-172971 JP; Y. Kitano, T. Ogawa, Y. Goto, and N. Yoshida, Chem. Abstr., 104, 88,588 (1986).
9. Kokai Tokkyo Koho 61-33177 JP; N. Kitano, T. Ogawa, Y. Furukawa, and N. Yoshida, Chem. Abstr., 105, 105,921 (1986).

10. N. Yoshida, K. Kitano, Y. Furukawa, T. Ogawa, S. Sugimori, Y. Goto, T. Isoyama, and K. Nigorikawa, Japanese Patent No. 186,045 EP; Chem. Abstr., 105, 181,666 (1986).
11. Kokai Tokyo Koho 60-25973 JP; Ref. Zh. Khim., 24N241P (1985).
12. Z. Arnold, J. Sauliova, and V. Krchnak, Coll. Czech. Chem. Commun., 38, 2633 (1973).
13. T. A. Kizner, M. A. Mikhaleva, and E. S. Serebryakova, Khim. Geterotsikl. Soedin. (in press).
14. W. Schäfer and H.-J. Deutscher, Z. Chem., 22, 447 (1982).
15. L. A. Karamysheva, E. I. Kovshev, and V. V. Titov, Zh. Org. Khim., 12, 1508 (1976).
16. G. Li, R. Yan, Y. Xiao, and W. Zhang, Huadong Huagong Xueyuan Xuebao, 11, 479 (1985); Chem. Abstr., 106, 130,999 (1987).
17. S. Patai (ed.), The Chemistry of Functional Groups. Suppl. A. The Chemistry of Double-Bonded Functional Groups, Wiley, London—New York (1977), Part 1, p. 112.
18. M. A. Mikhaleva, G. A. Kolesnichenko, and V. P. Mamaev, Izv. Sib. Otd., Akad. Nauk SSSR, Ser. Khim. Nauk, Vyp. 2, No. 5, 109 (1988).
19. D. Vorländer, Z. Phys. Chem., A126, 449 (1927).
20. H. Schubert, H.-J. Lorenz, R. Hoffmann, and F. Franke, Z. Chem., 6, 337 (1966).
21. H. Schubert and H. Zaschke, J. Prakt. Chem., 312, 494 (1970).
22. H. Zaschke, Wiss. Z. Univ. Halle, Math.-Naturwissensch. R, 29, 35 (1980).
23. H.-J. Hoffmann and P. Birner, J. Prakt. Chem., 327, 937 (1985).
24. H. Zaschke, J. Prakt. Chem., 317, 617 (1975).
25. G. Winter and H. Hartung, Mol. Cryst. Liq. Cryst., 149, 17 (1987).

SYNTHESIS OF 4-ALKYLTHIO-2-(o-HYDROXYPHENYL)-1,3,5-TRIAZINES BY RECYCLIZATION OF 4-OXO-1,3-BENZOXAZINE PERCHLORATES

Yu. I. Ryabukhin, O. B. Korzhavina, O. Yu. Ryabukhina, A. G. Gasanov, and A. D. Garnovskii

UDC 547.867.2.07'491.8.496.3:543.51'422

A method has been developed for synthesis of 4-alkylthio-2-(o-hydroxyphenyl)-1,3,5-triazines by treatment of 4-oxo-1,3-benzoxazine perchlorates with S-methyl, benzyl, and allyl-isothioureas.

sym-Triazines with different substituents in the 2-, 4-, and 6-positions have been little studied [1, 2]. These compounds (particularly the alkylthio derivatives) show high herbicidal activity [3] and the mono and di (o-hydroxyphenyl)triazines are used as highly efficient light stabilizers of polymers [4, 5] with specific spectral properties.

2,4-Dihydroxyphenyl-sym-triazines with alkyl(aryl) thio substituents are obtained by a Friedel—Crafts reaction of the chlorotriazines with resorcinol [4]. Mono(o-hydroxyphenyl)-triazines can be made either by fission of 2-(2-methylisoureido)- and 2-benzamido-4-oxo-1,3-benzoxazines with sodium methylate or thiophene [4] or by recyclization of 2-phenyl-4-oxo-1,3-benzoxazines with the S-alkyl-isothiourea [4, 6]. The latter method, however, is limited by the difficulty in obtaining benzoxazines, particularly the 2-alkyl derivatives which often cannot be prepared because of crotonic-type self-condensation [7, 8].

In our work the recyclization method of synthesis of the triazines is significantly modified by the introduction of the more reactive and readily available 4-oxo-1,3-benzoxazine perchlorates Ia-d [9-11] in the reaction with S-allylisothioureas. The possibility of using this method has previously been reported for the synthesis of 2-methylthio-4,6-di-(o-hydroxyphenyl)-sym-triazine [12].

As a result we have obtained the previously unknown 4-alkylthio-2-(o-hydroxyphenyl)-1,3,5-triazines IIa-g.

Physical and Organic Chemistry Research Institute, Rostov State University, Rostov-on-Don 344104. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1658-1661, December, 1989. Original article submitted July 11, 1988.