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SYNTHESIS AND LIQUID–CRYSTALLINE PROPERTIES OF DERIVATIVES OF 5-AMINO-2-ARYLPYRIMIDINES OF THE STRUCTURALLY STABILIZED ANIL TYPE

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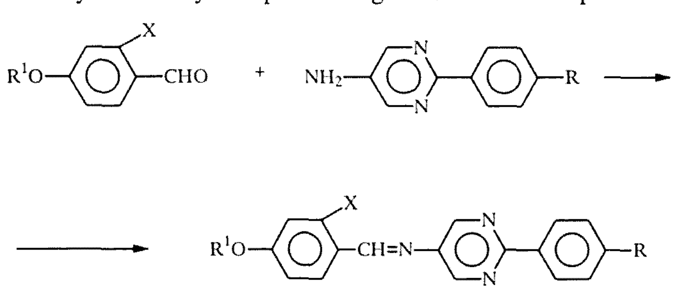
We have studied the liquid crystalline properties of the synthesized alkoxy-substituted 5-salicylidenamino-2-phenylpyrimidines compared with the corresponding benzylidene derivatives and as a function of the substituents.

Liquid crystals of the azomethine group have stimulated widespread interest owing to their properties which are of practical use (moderate phase transition temperatures and viscosity, good orientation on a substrate, etc.) [1-3], and their relatively low stability is compensated by the more advanced technology for manufacturing cells and the use of derivatives of salicyclic aldehyde: azomethines stabilized as a result of intramolecular hydrogen bonding [1, 4]. Derivatives of salicylidenanilines have been widely studied and represent one of the major classes of compounds which are actually used as a smectic C matrix [5, 6].

Among heterocyclic derivatives of liquid crystalline azomethines, only the pyridine derivatives have been systematically studied (for example, [7, 8]). Taking into account the practical importance of derivatives of 2-arylpyrimidines as components of liquid-crystalline materials [6, 9], in this work we have continued the investigations of the little-studied azomethines 2-aryl-5-aminopyrimidines [10], synthesized their analogs containing an intramolecular hydrogen bond, and considered the effect of the structure of azomethines I on mesomorphic behavior.

Substituted 5-benzylidenamino-2-phenylpyrimidines (Ia-f) were synthesized by condensation of the corresponding 5-amino-2-arylpyrimidines with alkoxybenzaldehydes upon boiling in toluene in the presence of piperidine.



Ia-f

Ia,b,e $R = OC_4H_9$; Ib $R = OC_6H_{13}$; Id,f $R = C_6H_{13}$; Ia,b $R^1 = C_6H_{13}$; Ic,d $R^1 = C_9H_{19}$;
Ie,f $R = -CH_2CH(CH_3)CH_2CH_3$; Ia,b $X = H$; Ic-f $X = OH$

Additional investigations of the liquid-crystalline phase of the previously obtained smectic liquid-crystalline 5-(p-octyloxybenzylidenamino)-2-butyloxypyrimidine (II) [10] showed that its smectic mesophase is classified as the A type, while anils I with a 2-arylpyrimidine moiety tend toward formation of smectic C over a broad temperature range in addition to smectic A. Compounds Ia,b have a smectic C range of about 80°C; and for compounds containing an intramolecular hydrogen

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TABLE 1. Mesomorphic Properties of Anils Ia-f

Compound	R^1	R	X	Phase transition temperatures, °C				Yield, %
				K-S_C	S_C-S_A	S_A-N	N-I	
Ia	C_6H_{13}	OC_4H_9	H	108,9	183,5	213,0	241,5	[10]
Ib	C_6H_{13}	OC_6H_{13}	H	107,1	185,5	214,4	230,1	[10]
Ic	C_9H_{19}	OC_4H_9	OH	104,7	235,5	250,6	251,5	73
Id	C_9H_{19}	C_6H_{13}	OH	82,9	218,5		231,0	85
Ie	C_5H_{11}*	OC_4H_9	OH	191,2*		204,3*	234,5	82
If	C_5H_{11}*	C_6H_{13}	OH	177,3*	184,7	206,7*	209,2	80
II				85,9		177,3		[10]

TABLE 2. Heats of Phase Transitions of Anils Ic,d

Compound	ΔH°, kcal/mole		
	K-S_C	S_C-S_A	N-I
Ic	6,72		1,45
Id	8,11	0,14	2,07

bond (Ic,d), the range of the smectic C mesophase is expanded to 130°C. This expansion occurs mainly as a result of the increase in thermal stability. The trends found in the appearance of liquid–crystalline properties by salicylidenaminopyrimidines are consistent with those noted in the literature for salicylidenanilines: enhancement of the mesogenic properties as a result of the increase in anisotropy of the electronic polarizability due to electron delocalization over the aromatic and chelate rings [11, 12] and the increase in the tendency toward appearance of a smectic phase due to flattening of the molecule, caused by the decrease in the angle of rotation of the N-aryl group when an intramolecular hydrogen bond is present [11, 13].

Introducing a 2-methylbutyl group (a widely used fragment for constructing low-melting smectic C^* molecules [1, 5]) into the salicylidenaminopyrimidine molecule negatively affected the liquid crystalline properties. In the anils Ie, f, the transition temperature to the mesophase (T_{mp}) was considerably elevated and as a result there occurred a marked narrowing of the ranges of both the mesomorphic state as a whole (up to 30-40°C) and of the smectic C in particular (up to 7-13°C). In contrast to the dialkoxyanils Ia-c, the derivative Ie does not have a smectic A mesophase.

In the *ortho*-hydroxy derivatives Ic,d,f, suppression of the appearance of nematics occurs with enhancement of the appearance of the smectic properties: in anils Ic,f we observe considerable narrowing of the interval of the nematic mesophase (to ~ 1°C) and even its disappearance in the alkylalkyl derivative Id.

For salicylidenaminopyrimidines Ic,d, we measured the heats of the phase transitions crystal–S_C, S_C–S_A, and N–I, but for compound Ic the transition S_A–N could not be measured due to the proximity of the N–I transition to it.

EXPERIMENTAL

The phase transition temperatures, the types of mesophases of the anils Ia-f, II and the heats of the phase transitions of anils Ic,d were determined by thermal microscopy on a Mettler FP-52 heating stage with the polarizing microscope POLAM-211 and the Setaram DSC-111 differential scanning microcalorimeter. The UV spectra were taken on the Specord UV-Vis spectrometer in alcohol. Symbols used: K – crystal, S – smectic, N – nematic phase, I – isotropic melt.

The elemental analysis data for anils Ic-f correspond to the calculated values.

2-(p-Butyloxyphenyl)- and 2-(p-hexyloxyphenyl)-5-aminopyrimidines [10], 2-(p-hexylphenyl)-5-aminopyrimidine [14], p-alkoxysalicylic aldehydes [15], and (S)-p-(2-methylbutyloxy)salicylic aldehyde[5] were synthesized according to the techniques described previously.

Synthesis of Azomethines Ic-f. A mixture of 3.4 millimoles 5-amino-2-arylpyrimidine and 3.4 millimoles substituted benzaldehyde was boiled for 5-6 h in 10 ml toluene with 3 drops piperidine. The hot solution was filtered and cooled down to 10-15°C. The residue was filtered and compounds Ic,d were recrystallized from a 10:1 alcohol–toluene mixture, and compounds Ie,f were recrystallized from a 1:1 benzene–methanol mixture. UV spectra, λ_{max} (lg ε): anil Ic 210 (4.02), 312 inflection (3.90), 367 nm (4.12); anil Id 206 (4.52), 30.6 (4.39), 362 nm (4.48).

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