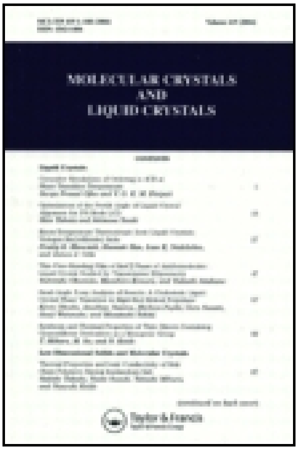

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Synthesis of Pyrimidyl Ethane Derivatives and their Properties in Mixtures

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SYNTHESIS OF PYRIMIDYL ETHANE DERIVATIVES AND THEIR PROPERTIES IN MIXTURES

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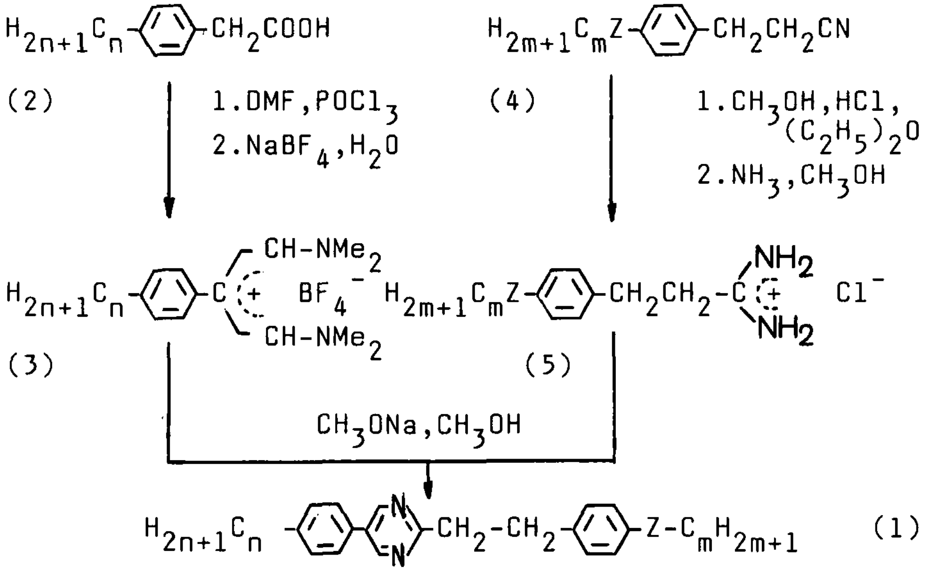
Abstract 1-(5-(4-alkyl- or phenyl)pyrimidyl-2)-2-(4-alkyl or alkoxyphenyl)ethanes were synthesized and their binary mixtures with 4-alkoxyphenyl 4-alkoxybenzoates were investigated by microscopic, calorimetric, X-ray and dielectric methods. A new kind of smectic A phase has been observed above the smectic C phase which has given an unusually high didifraction peak.

INTRODUCTION

Alkyl- and alkoxyphenylpyrimidines being smectics C become again the object of interest.[1] Binuclear phenylpyrimidines have fairly low S_C-S_A and S_C-N phase transition points, whereas in trinuclear diphenylpyrimidines the S_C phase is often preceded by one or more phases of higher ordering (S_G or S_F).[2] We decided to investigate how will the phase situation be affected in trinuclear pyrimidines if the rigid core of the molecule is separated by introducing a flexible ethylene spacer.

SYNTHESIS

Several compounds of formula (1) have been synthesized in which Z denotes an oxygen atom or a single bond as it is shown in the scheme below:



This synthesis was based on the results of an earlier work in which the pyrimidine ring was obtained as a result of condensation of amidine hydrochloride and bis (dimethylamino) 2-arylpropenium tetrafluoroborate. This procedure is much simpler as compared with other methods^{3,4} in view of the availability of the intermediates used and high yield, which amounted in the case of compounds (1) to about 80%. More preparative details can be found in our earlier work.^{5}

MESOMORPHIC PROPERTIES

The phase transition temperatures and enthalpies of compounds (1), determined by the thermomicroscopic and DSC methods, are summarized in Table I. The obtained compounds: the dialkyl- and alkyl-, alkoxy- derivatives reveal the presence of orthogonal smectic phases A, B_{hex} and E. The phase S_C was not detected, despite it is present in the analogue of (1b) without $-CH_2-CH_2-$ spacer^6. It is probably due to the fact that the introduction of the ethylene bridge increases the rotation ability of the molecule or its fragments about the long axis.

In compounds (1a) and (1b) the phases have been identified by the X-ray method and subsequently confirmed by mixing with standard compounds.

Table I The phase transition points (upper line, °C) and enthaplies (lower line, kcal mole^{-1}) of compounds (1)

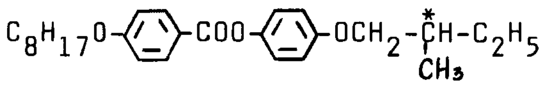
No	m	n	Z	C_1	C_2	S_E	$S_{B_{hex}}$	S_{A_1}	I
1a	6	6	-	* 61 (1.14)	* 75.8 (0.08)	* 77.5 (3.5)	* 98 (0.65)	* 121 (2.1)	*
1b	6	6	0	-	* 95.5 (49)	-	* 103.2 (0.5)	* 131.5 (1.9)	*

Binary mixtures with the smectic C compounds

Though compounds (1) are not smectics C we assumed that in mixtures they may reveal virtual smectic C properties and may be considered as components of mixtures for compounds with a smectic C phase. To verify this concept we determined phase diagrams of mixtures of compound (1b) with esters (6) and (7), the former revealing the smectic C phase, and the latter the chiral smectic C phase:

(6)

C 60.5 S_C 66.5 N 90 I



(7)

C 42 (S_B21) S_C 44 S_A 60 I

In the case of the (1b-6) binary system, Fig.1a, the S_C phase occurs in a wide concentration range and its thermal stability is even somewhat increased to compare with (6). As regards the (1b-7) binary system, Fig.1b, the stability of the S_C phases is slightly lower.

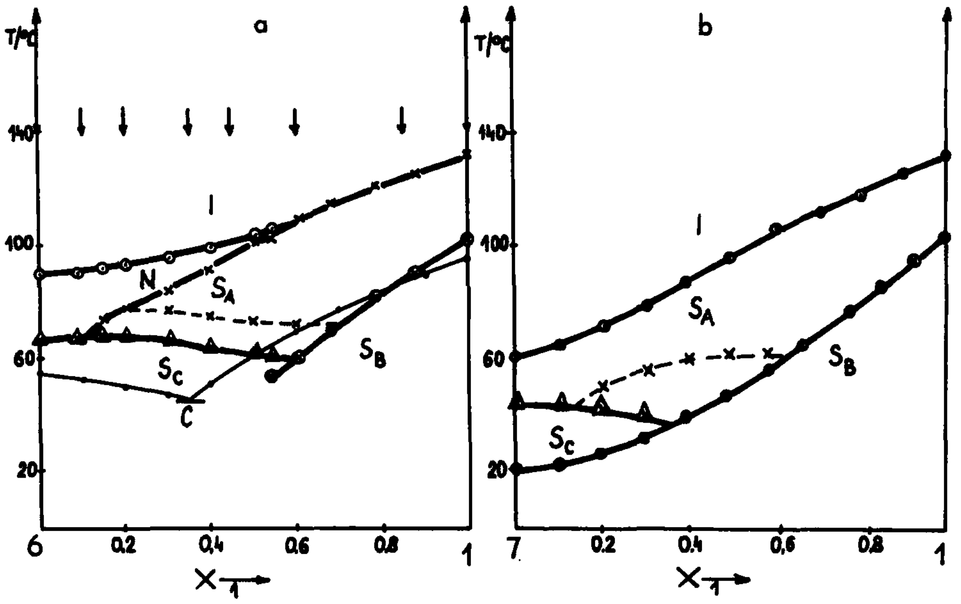


Figure 1 Phase diagrams of binary mixtures composed of (1b and 6) - a and of (1b and 7) -b. The dashed lines present the S_{A_1} -S_{A_x} phase transitions found on the basis of change of texture observed under the polarization microscope. The vertical arrows in Fig. 1a denote that for the given compositions the intensities of the Bragg peak have been measured as well as the smectic layer spa-

cings as a function of temperature of samples ordered in a magnetic field of 0.6 T.

It has been found that beginning from the composition of X_6=0.07 mole ratio to that of X_6=0.6 in the temperature range of a dozen or so degrees above the S_C-S_{A_1} phase transition point the intensity of the Bragg peak is by one order of magnitude greater than that observed for the S_C or S_{A_1} and S_B phases in the pure compounds or in their mixtures beyond the mentioned range of concentrations (see Fig. 2a and 2b).

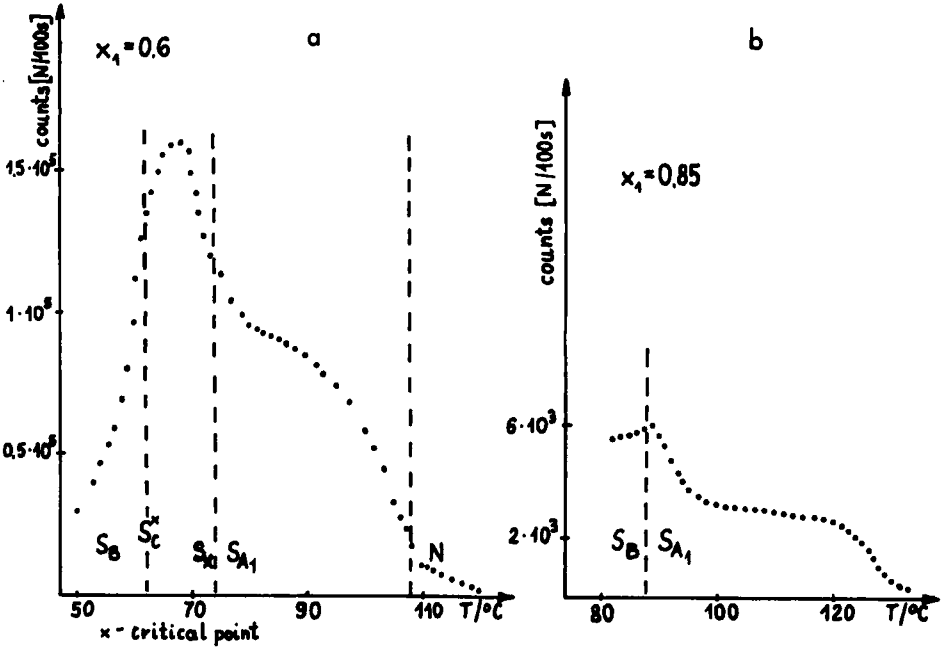


Figure 2 Intensity of the Bragg scattering of X-rays as a function of temperature for (1b-6) binary mixtures of the compositions: X_6=0.6 - a and X_6 =0.85 - b .

Microscopic observations of the samples of mixtures placed between unidirectionally rubbed microscopic slides reveal small changes of the fan texture on cooling, consisting in the blackening of the sides of the fan and the straightening of the fan edges similar to that observed for the S_{A_1}-S_B transition at the temperature corresponding to the rapid increase of the Bragg peak intensity. One can therefore believe that there exists a S_{A_x}-S_{A_1} transition between the two regions of smectic A differing as regards the degree of ordering. In the S_{A_x} region we observe a greater smectic layer spacing than in the S_{A_1} region. The mentioned transition is not observed, however, by the DSC method. Also the conductivity of the smectic layer ordered in an electric field (both the parallel and vertical components) shows only monotonic changes. In distinction, the vertical component of electric permittivity $\varepsilon_\perp$ assumes maximal values at the S_{A_1}-S_{A_x} transition point what may indicate that the ability of the molecule or its fragments to rotate is different in both these phases. It remains to decide whether the S_{A_x} phase is really a higher ordered modification of the S_{A_1} phase, or whether it is a normal S_{A_1} phase more liable to ordering. It would be interesting to know in what mixtures the S_{A_x} phase may be observed? Is it specific for compounds in which the C phase occurs between the B and A_1 phases?

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