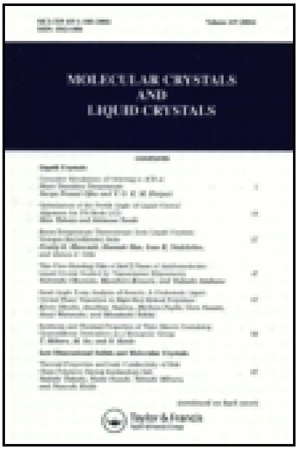

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Smectic B and E Phases Induced in Hydrogen-Bonded Associates

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Smectic B and E Phases Induced in Hydrogen-Bonded Associates

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Smectic phases are obtained by self-organization of proton acceptors and donors which fulfil the two conditions: a suitable pK_s-value of the carboxylic acid and a molecular shape of the associate which is able to form mesophases. Following this concept associates with smectic B phases and at the first time the crystalline S_E modification were designed. The existence of the phases was proven by calorimetric, microscopic and X-ray investigations.

Keywords: Hydrogen bonds; rod-like molecules; smectic B phase; smectic E phase; phase diagrams; X-ray investigations

1. INTRODUCTION

It is well known that hydrogen bonds are able to form intra- and intermolecular associates. The main feature of this bond is that the free electron pair of the proton acceptor (**A**) and the orbital of the proton of the donor (**D**) try to be maximal overlapped. Therefore, hydrogen bonds are acting in a preferred direction.

Furthermore, the intensity of the interaction in the complex D-H···A depends on the polarity of both, **D** and **A** [1].

By suitable selection of the components associates can be obtained with a sufficient length-to-breadth relation. Such singular associates form liquid

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crystalline phases [2] as it was observed in derivatives of benzoic and cyclohexanecarboxylic acids [3–5], carboxylic amides [6], pyridones [7] as well as in mixtures of different pyridines with phenols [8–9] and acids [10–18].

Specially the last mentioned case, investigated at the first time by Kato and Frechet, is of interest because the singular associates are stable and can be isolated as chemical compounds [10]. In most of the associates layered liquid crystalline phases (S_A, S_C) and nematic phases (N) were detected. Only one example is known where a S_B phase was identified [15].

Recently Bernhardt *et al.* [19] show that the stability of the liquid crystalline state depends on the Hammett constant of the substituted benzoic acids. This idea, to use proton donor and acceptor systems with optimal bonding power, was the key to create building units which are able to form stable liquid crystalline phases of different types.

Furthermore, as trick the —COOH···N— fragment, forming the hydrogen bridge, was substituted by an —COO— unit. When the corresponding esters show crystalline[◆] S_E phases one can expect for the associates the analogous behaviour, too.

2. EXPERIMENTS AND RESULTS

Firstly, we synthesized as proton acceptor **A1** 4-(4-*n*-octyloxyphenyl) pyridine (cr 337 I) using common methods [20] and mixed it with palmitic acid **D1** (cr 337 I). **D1** was chosen to re-create 4-(4'-*n*-octyloxybiphenyl) myristate known for the existence of highly ordered phases: cr 355 S_G 377 S_F 381 I [21]. We have found in the binary system **A1** and **D1**, shown in Figure 1, the induction of thermodynamically stable liquid crystalline phases (S_A and S_B) by microscopic observation. Furthermore, the existence of a metastable crystalline smectic E phase was observed.

The texture of the induced S_E phase is shown in the microphotograph of Figure 2. Due to the different light intensities the homeotropic orientated parts of the former S_B-phase seem to be uniaxial (Fig. 2a). But higher times of exposure prove that the homeotropic oriented S_B-phase transforms into a texture shown in Figure 2b. It should be emphasized, that all investigated samples exhibit a strong tendency for homeotropic orientation. Therefore,

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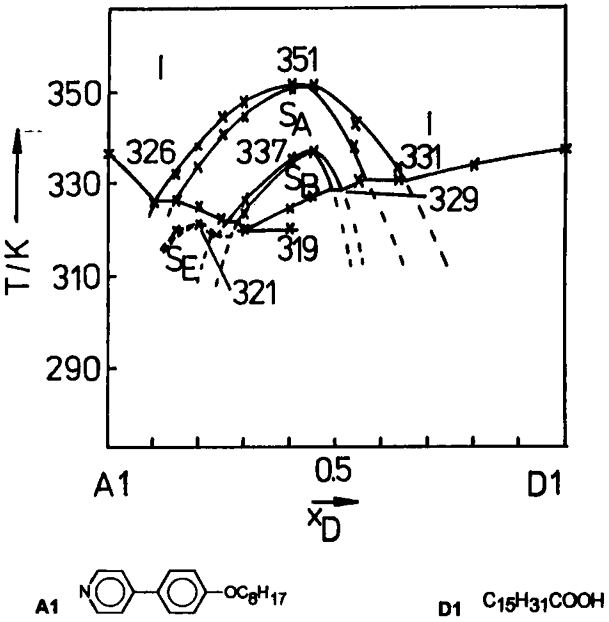
[◆] We use term "crystalline" in order to differentiate between a hexatic (2D) and a three dimensional order. It should be emphasized that it cannot be compared with a real crystal because the rotations, specially the reorientation around the short and long axis, have been proven to exist in the S_E phase.



D1 $C_{15}H_{31}COOH$

FIGURE 1 Diagram of the binary system A1 and D1.

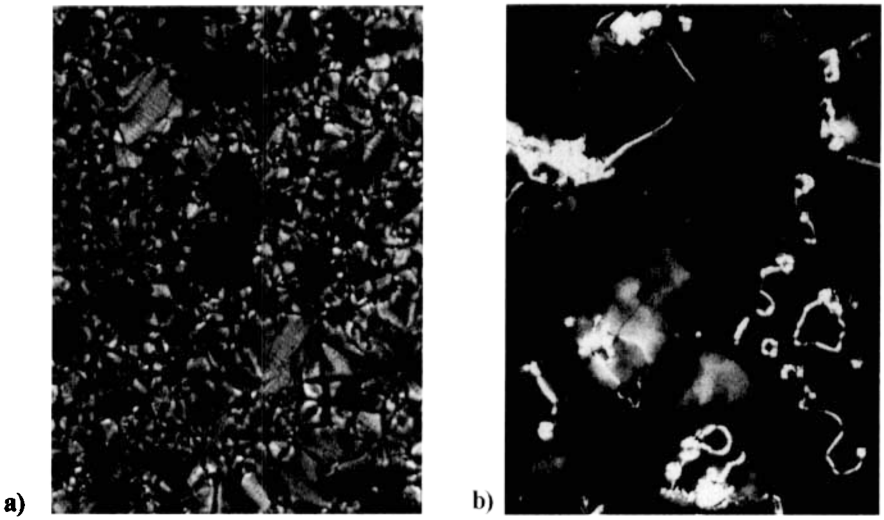


FIGURE 2 Microphotographs of the S_E-phase (original magnification 200 ×) a) planar orientation b) homeotrophic orientation.

the transitions have been additionally checked by calorimetric measurements (DSC-7, Perkin-Elmer).

In order to reach stable S_E phases the proton acceptor was extended to 4-(4-*n*-hexyloxybiphenyl-4′-oxymethyl) pyridine **A2** (cr 429 I) [22] which itself do not show a liquid crystalline phase. As proton donor the nematic (N) hexyloxybenzoic acid **D2** (cr 380 N 425 I) was added. The results of the calorimetric investigations for the first heating runs of different mixtures are presented in Figure 3. Some transitions cannot be clearly seen due to the comprehensive presentation of the data. The following discussion is related to DSC-traces with a higher enlargement.

For the interpretation of the low temperature part between $0 < x_{D2} < 0.5$ one has to consider the solid-solid transition of **A2** at 356 K. Therefore, the second eutectic point at about 370 K is not so sharp. An interesting effect is observed at the DSC-trace at $x_{D2} = 0.25$. There are peaks at 355 K (solid-solid transition), 369 K (eutectic point), 382 K (broad), 418 K, 425 K (intensive) and a broad between 435 and 445 K (clearing process). By microscopic investigations the phase from 418 K to 425 K was identified to be a S_B phase. The phase below 418 K exhibits the same texture as shown in Figure 2 and therefore it was denoted as crystalline S_E.

At concentrations $x_{D2} > 0.5$ an eutectic point at about 370 K was detected. At $x_{D2} = 0.5$ a melting process at about 395 K and two sharp phase transitions at 435 and 457 K were found. The respective phases showing homeotropic and fan-shaped textures are related to the S_A and S_B phases.

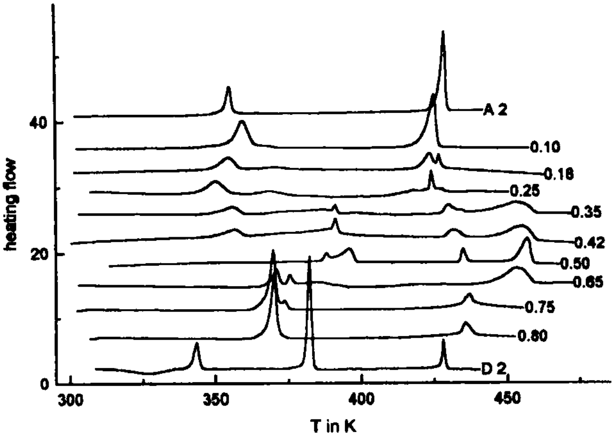


FIGURE 3 DSC-traces (1st heating run) of all mixtures of the system **A2** and **D2** and the pure substances **A2** and **D2**. The numbers are related to the molar fraction of **D2**.

Much more complicated is the DSC-trace at $x_{D2} = 0.65$ which is not completely resolved in Figure 3. Again an eutectic point at 370 K, a sharp phase transition at 376 K, and a broad transition range between 378 K and 397 K (weak) were detected. Further peaks were measured between 420 K – 429 K (weak) as well as between 445 K and 455 K (stronger).

The whole phase diagram obtained by a combination of microscopic and calorimetric investigations is presented in Figure 4.

The microphotograph in Figure 5 shows the coexistence of different phases in the system **A2** and **D2** at 394 K. It has been proven by microscopic investigations using the contact preparation that a smectic C phase exists above 373 K and transforms at about 405 K into S_A.

It is well known that trans-4-*n*-octylcyclohexylcarboxylic acid (**D3**) (cr 310 S_B 363 N 371 I) exhibits a smectic B phase [23]. Previous investigations have shown that the S_B phase disappears by adding a second component [8]. In order to stabilize the higher ordered phases, **D3** was added to 4-(4-*n*-hexyloxybiphenyl-4′-oxymethyl) pyridine **A2**.

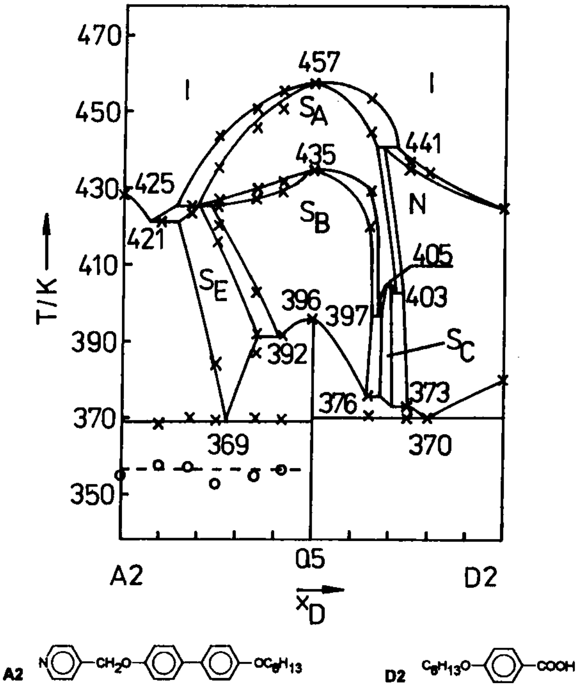


FIGURE 4 Phase diagram of the system **A2** and **D2**.

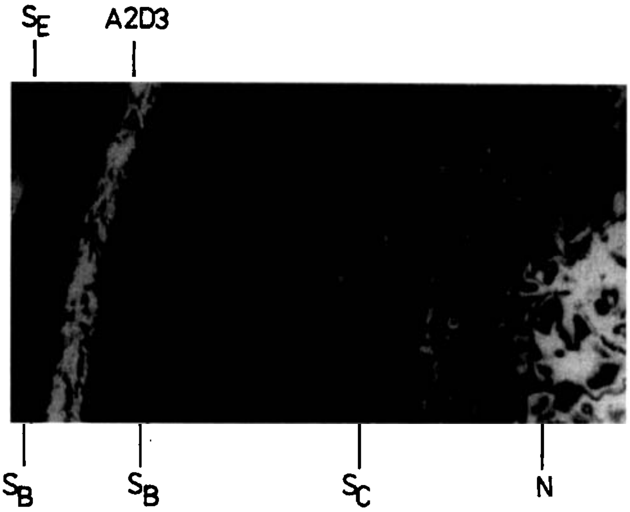
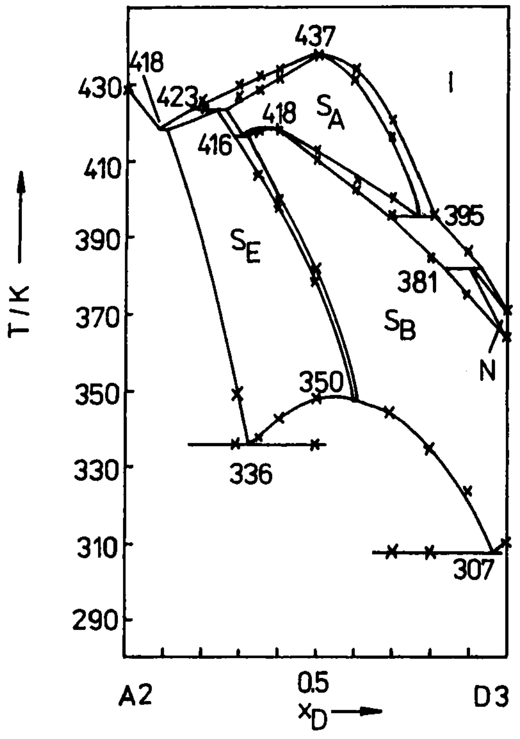


FIGURE 5 Microphotograph of the system **A2** and **D2** at 394 K (original magnification 200 ×).

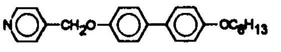
The phase diagram (Fig. 6) proven by microscopic and calorimetric measurements shows the existence of an 1:1 associate in the solid state, the destruction of the nematic and stabilization of the S_B phase as well as the induction of the S_A and S_E phases. Specially, the crystalline S_E phase is stabilized in the mixture between the 1:1 associate and **A2**. It should be pointed out that for the singular associate an enantiotropic crystalline S_E phase was detected. X-ray measurements were carried out to confirm this finding. The reflections observed are listed in Table I.

An orthorhombic unit cell in the crystalline S_E-phase of $a = 0.816$ nm, $b = 0.548$ nm and $c = 4.11$ nm was calculated from these data. Because of the orthorhombic structure it can be expected, that c agrees with the length of the building units ($L = c$). The c-value given above is in excellent agreement with the length of the associate **A2D3** ($L = 4.2$) nm estimated from molecular models.

Furthermore, X-ray measurements were performed at $x_{D3} = 0.35$. The X-ray pattern in Figure 7 yields to a d-value in the S_E-phase of $d = 3.6$ nm. This is much higher as expected for **A2** ($L = 2.44$ nm) and smaller than the length of the 1:1-associate **A2D3** with $L = 4.1$ nm. To explain this result d was estimated using the rule of additivity of the corresponding components [24], **A2** and **A2D3**: $L_{0.35} = 0.30{*}L_{A2} + 0.70{*}L_{A2D3}$.



A2



D3

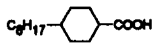


FIGURE 6 Phase diagram of the system **A2** and **D3**.

TABLE I θ-values for the singular **A2D3** and the d-values calculated via the θ-values

T in K	*θ-values in °*	*d-values in nm*
363	1.074	4.11
	2.134	2.07
	9.754	0.45
	10.890	0.41
	13.654	0.33

Thereby the molar fractions are related just to this part of the phase diagram, that means $x = 0.35$ in diagram 7 is transformed into the mole fraction of the associate $x' = 0.70$. The result of $L_{0.35} = 3.6$ nm agrees well with the X-ray findings and indicates that there exists a mixture of **A2** and the 1:1 associate at the given concentration.

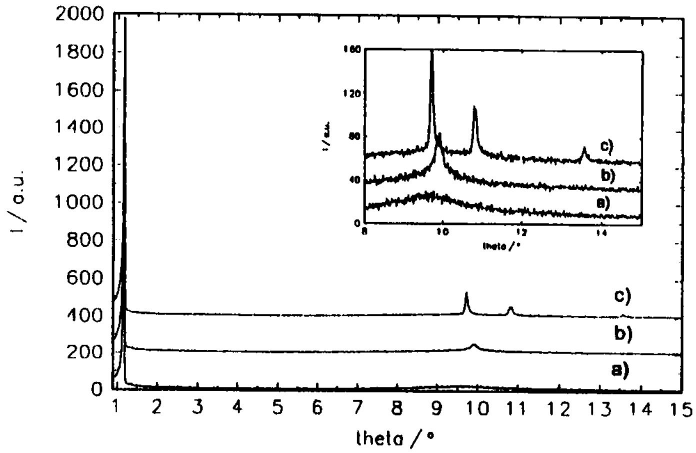


FIGURE 7 X-ray results of the Guinier-method of the mixture $x_{D3} = 0.35$ of the system **A2** and **D3**, inserted part: intensity from 0 to 160 and theta from 8 to 15° a) smectic A phase at 423 K; b) smectic B phase at 413 K; c) smectic E phase at 393 K.

Summarizing the experimental data we can establish that by use of suitable combinations of the proton donors and acceptors associates with smectic low temperature phases can be obtained.

Acknowledgements

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