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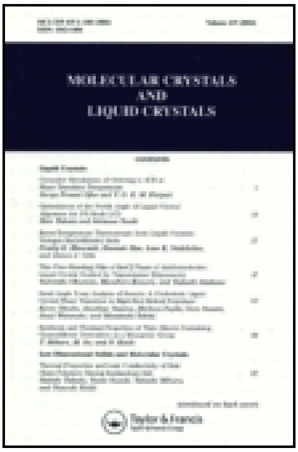

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Hydrogen Bondings and LC State

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HYDROGEN BONDINGS AND LC STATE

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Abstract Hydrogen-bonded associates with a swallow-tailed and a chair-like molecular shape are produced in binary mixtures using different proton donators and acceptors.

INTRODUCTION

Hydrogen bondings are interactions which strongly depend on the mutual position of the proton donator P and acceptor A. Therefore, they are able to structure the condensed matter. Such effects can be observed in simple liquids like water or in complicated biological systems e.g. in helical DNS molecules[1]. A typical feature of hydrogen bonded aggregates in the liquid state is the dynamics which is very important for biological processes. In order to simplify the situation liquid crystalline samples can be used because stabilization and destabilization of the respective phases strongly depend on the molecular shape. For this reason simple derivatives of 4-subst. benzoic- or cyclohexanecarboxylic acids exhibit mesomorphic phases[2-4]. On the other hand in binary systems mixed associates of different acids can be produced which can stabilize the liquid crystalline state. Furthermore such associates can have a longitudinal dipole which can be used to prove by dielectric relaxation measurements the existence of the aggregates[5]. In the mean time a lot of di- and trimeric associates formed by the free electron pair of a nitrogen containing compounds and organic acids[6-11] or phenols[12,13] including enamineketones[14,15] were published. In all this cases the authors tried to produce associates with a high length-to-breadth ratio in order to stabilize the phase range of the liquid crystalline state. There are only few attempts to vary the molecular shape[12,13]. Therefore, we have carried out mixing experiments on components with a swallow-tailed shape or a big lateral substitution.

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RESULTS

The investigations were done using a heating stage polarizing microscope. At first the general phase behaviour of the mixtures (eutectic temperatures, three phase reaction, maxima and minima of two phase lines) was investigated by the contact method[16]. If no topological specialities were observed the phase diagrams were sketched only by these data In the other case the diagram was proven by the aid of single concentrations. Sometimes the samples were annealed about one hour at a certain temperature to obtain a thermodynamically stable phase.

Associates with swallow-tailed structure

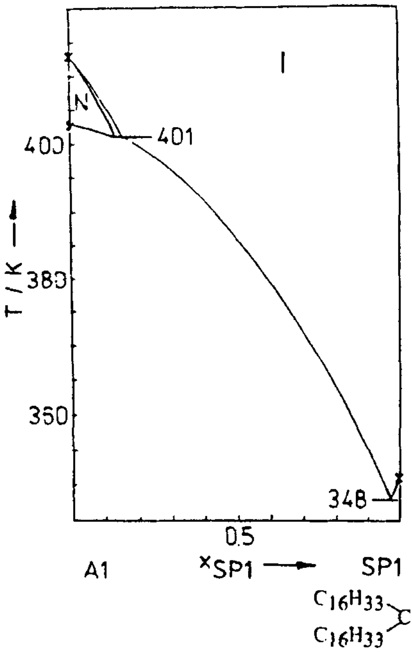
In the first part associates with a swallow-tailed structure were produced.

There are three possibilities

i a swallow-tailed proton donator SP can be mixed with a linear pyridine derivative A,

ii the swallow-tailed part is connected with the pyridine derivative SA as acceptor,

iii P and A are swallow-tailed compounds SP-SA or a swallow-tailed acid/pyridine aggregated with a bipyridine to $(SP)_2AB$ or with a bifunctional acid to $PB(SP)_2$.



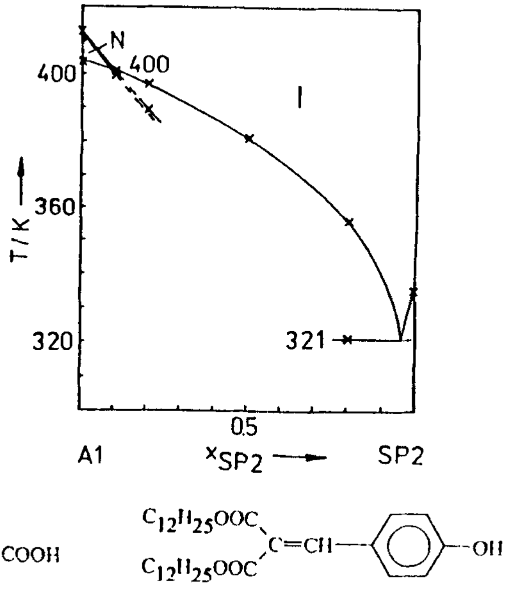


Fig. 1 Phase diagram of the linear pyridine A1 and the swallow-tailed acid SP1 as proton donator. Eutectic and three phase temperatures T/K are given

Fig. 2 Phase diagram of A1 and the phenol derivative SP2

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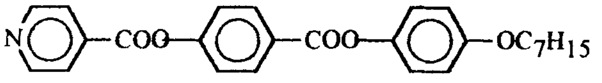
The first case i can be realized in mixtures of 4(4-n-heptyloxyphenyloxycarbonyl)phenyl pyridine-4-carboxylate with terminally branched aliphatic carboxylic acids (Fig. 1) or phenols (Fig. 2) as proton donator.



A1

cr 403 N 413 I (temperatures in K)

In both cases a destabilization of the nematic phase can be detected. The molecular shape as well as the donator intensity of SP1 can be changed by introduction of a benzene unit. Using of 4-[2,2-bis(tetradecanyloxycarbonyl)ethenyl]benzoic acid in combination with A1 results in a stabilization of the nematic state and an introduction of the smectic A phase as shown in Fig. 3.

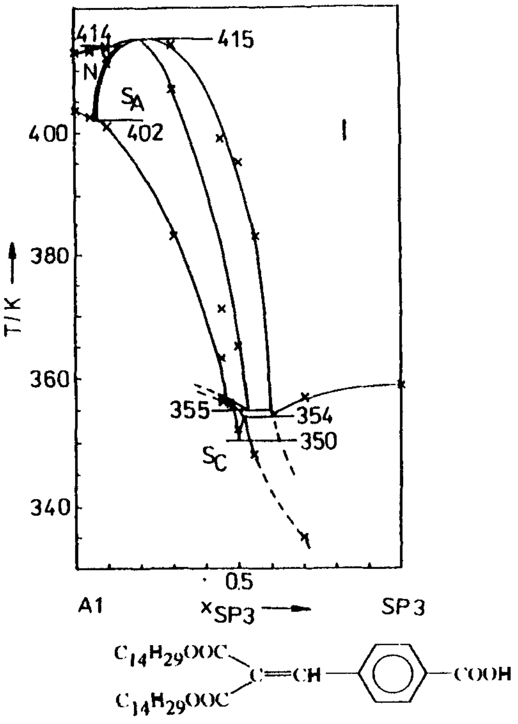


Fig 3 Phase behaviour of the swallow-tailed acid SP3 and the proton acceptor A1

The maximum of the clearing temperature was detected at the molar fraction x(SP3)~0.2 indicating the strong tendency of the swallow-tailed acid SP3 to destroy the 1:1 associate. A solid compound which can be related to the associate was not detected in the phase diagram.

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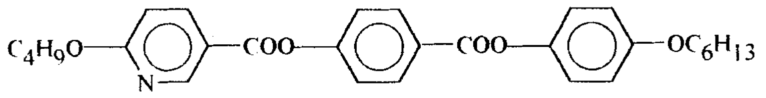
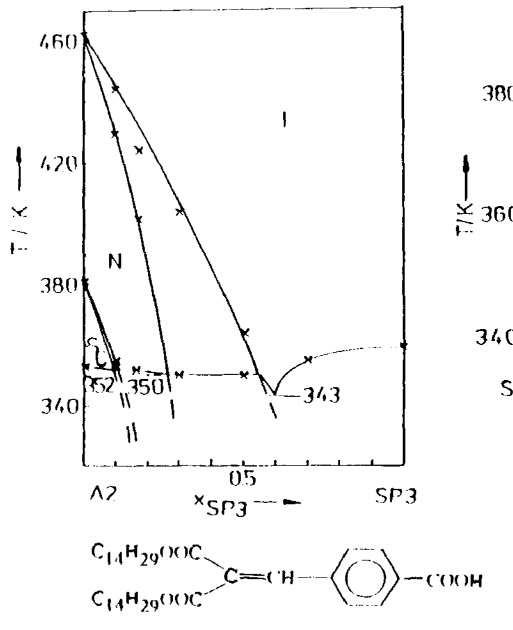
The shape of the associate is strongly changed if 4-[4-n-hexyloxyphenyloxycarbonyl)-phenyl] (6-n-butyloxy)pyridine-3-carboxylate is used as acceptor.



A2

cr 351 S_C 381 N 462 I

As shown in Fig. 4 no stabilization of the liquid crystalline state of A2 could be observed by addition of the benzoic acid derivative SP3. The angled shape of the associate destroys the nematic as well as the tilted smectic C phase.



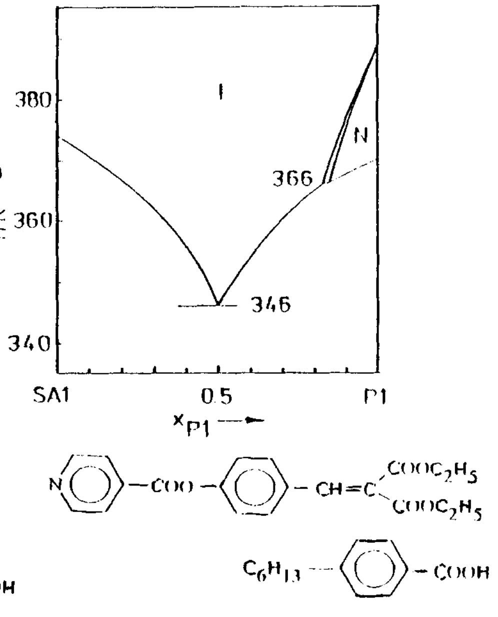


Fig. 4 Phase diagram of the derivative of nicotinic acid A2 and of the swallow-tailed acid SP

Fig. 5 Phase diagram of a swallow-tailed pyridine with 4-n-hexylbenzoic acid

Generally the same situation is observed if the -COOH group of SP3 is substituted by an -OH one. In this case also a broad two phase range N/I was detected indicating a strong tendency to destroy the liquid crystalline order (diagram not presented). First investigations of the combination P/SA with a swallow-tailed pyridine derivative also results in a destruction of the mesomorphic state (Fig. 5).

Diswallow-tailed associates can be expected in the above given combinations iii. The mixture

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of 4,4'-bipyridyl AB as a bifunctional acceptor with the swallow-tailed acid SP3 results in a simple double eutectic system as demonstrated in Fig. 6. The maximum of the melting curve at 366 K is related to the solid compound AB (SP3)$_2$. In the opposite case glutaric acid PB was mixed with the given swallow-tailed pyridine. Neither the induction of a liquid crystalline phase nor a maximum of the melting curve was detected (Fig. 7).

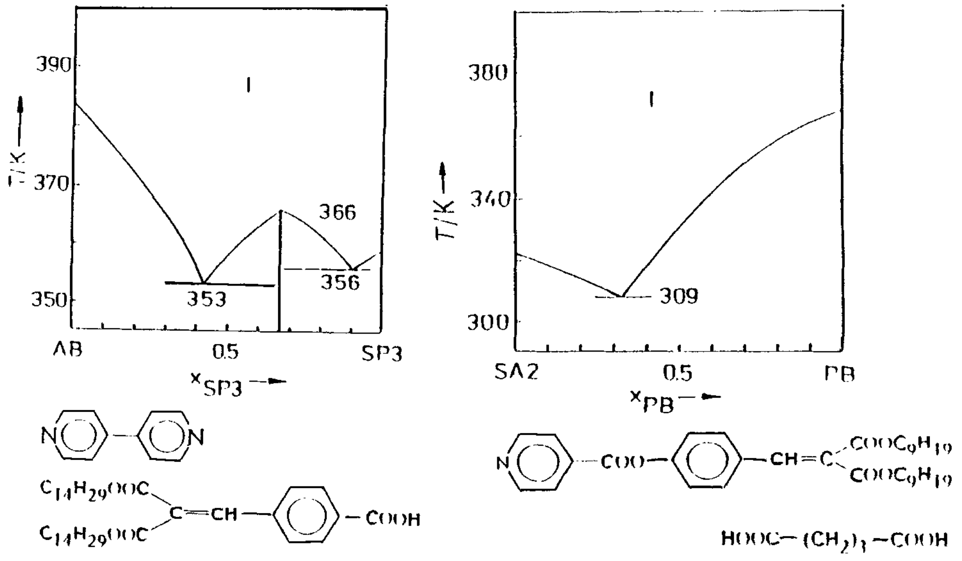

Fig. 6/7 Two attempts to obtain di-swallow-tailed associates by a bifunctional acceptor and monofunctional proton donators (Fig. 6) and vice versa (Fig. 7).

Summarizing the data from phase diagrams one can conclude that the stabilization of the nematic and induction of the S$_A$-phase only could be observed in associates which contain four benzene units in contradiction to the well known swallow-tailed compounds[17] consisting of three phenylene rings. To obtain bi-swallow-tailed associates further investigations are necessary.

Associates containing a chair-like proton donator CP

At first Weissflog et al. reported about "chair-like" molecules with liquid crystalline phases[18]. For our experiments we used the chair-like acid CP which forms dimers in the liquid crystalline state. 3-(4-cyanobenzyloxycarbonyl)-4-(n-octyloxybenzoyloxy)benzoic acid CP represents a novel type of strongly branched liquid crystalline benzoic acids[19]. They are dissociated and elongated by addition of the linear pyridine A1 as proton acceptor.

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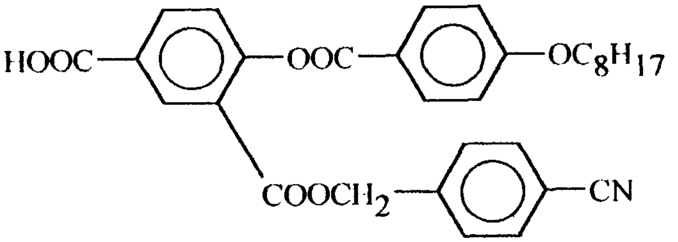
Consequently an increase of the clearing temperatures and a strong stabilization of the S_A phase should be found.



CP

cr 420 (S_A 418) N 429 I

This can be seen in the phase diagram of Fig. 8. We have had problems to find the melting curve or to detect a maximum in the melting curve. May be that the associate CPA1 must be strongly supercooled to crystallize. In contradiction to the former experiment and the data

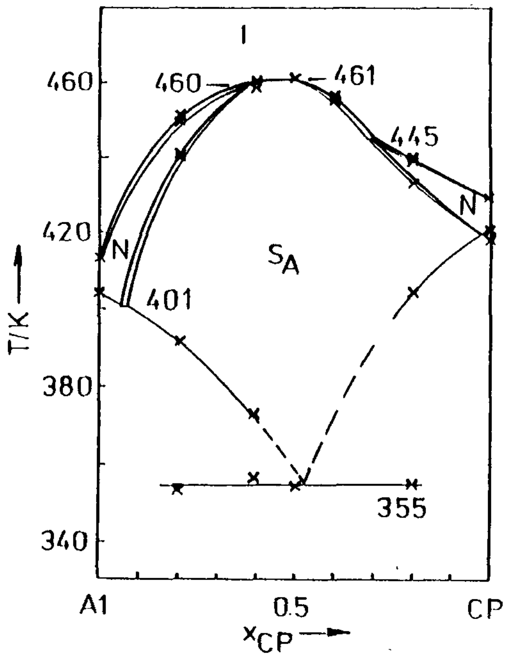


Fig. 8 Phase diagram of CP and proton acceptor A1

of Fig. 4 we have had no difficulties to crystallize the associate CPA2 by supercooling of about 10 K. Addition of the nicotinic acid derivative A2 results in the formation of a angled associate which forms only a nematic phase (Fig. 9). As mentioned before the dimeric CP

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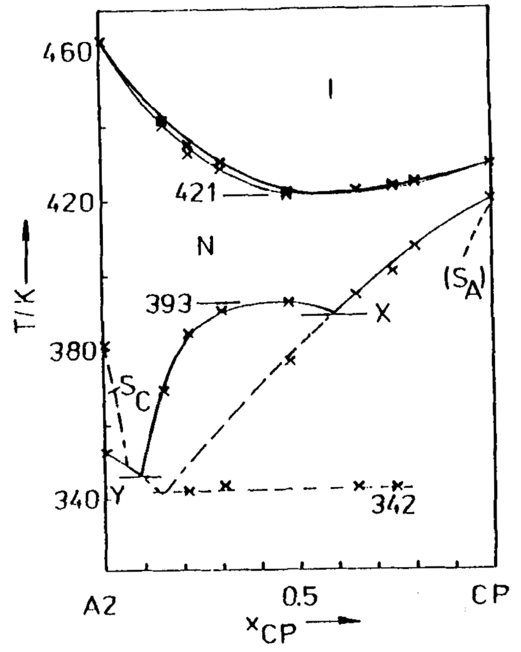
exhibit a nematic and a supercooled S_A phase. An elongation of the dimer can be obtained by addition of 4,4'-dipyridyl AB.



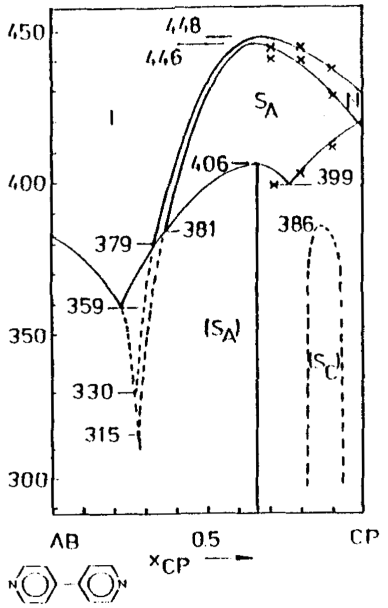


Fig. 9 Binary system of the chair-like acid CP as proton donator and the derivative of nicotinic acid as acceptor. The eutectic temperatures X and Y could not be exactly observed

Fig. 10 Phase diagram of CP with the double acceptor AB. Two phase lines are not given

Two eutectica and the maximum of the melting curve at T=406 K indicate the existence of the associate $(CP)_2AB$ with a small nematic and an extended S_A phase which could be supercooled down to 300 K (Fig. 10). The induction of a metastable smectic C phase at a 1:1 mixture of the dimer CP and the trimer $(CP)_2AB$ is an interesting feature of this phase diagram. All in all phase diagram 10 is a good example for the interaction of forces connected with hydrogen bondings and steric interactions. Therefore, additional investigations, especially X-ray and IR-measurements are necessary to know more about packing and dynamics in the presented associates.

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DISCUSSION

In both associates formed by hydrogen bondings, the swallow-tailed and the chair-like, an induction of a smectic phase and a stabilization of a nematic phase was detected The chair-like associates show a strong tendency to form stable dimers and trimers - an effect which especially can be seen by comparison of the associates with 4,4'-dipyridyl given in the Figs. 6 and 10. To obtain induced or stabilized mesomorphic phases in swallow-tailed associates an elongation of the donator or acceptor molecules seems to be necessary. Generally it can be realized that associates with stronger deviation from the rod-like molecular shape are able to stabilize the liquid crystalline state.

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