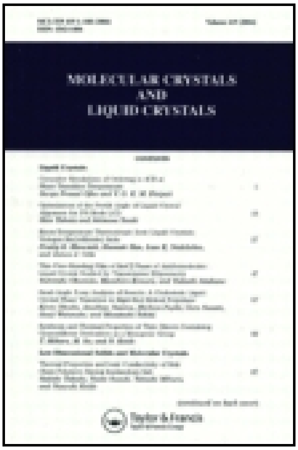

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Stabilization and Induction of Liquid Crystalline Phases by Hydrogen Bonds

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Stabilization and Induction of Liquid Crystalline Phases by Hydrogen Bonds

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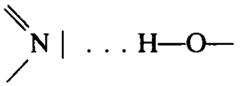
The formation of induced liquid crystalline phases by hydrogen bonds between nitrogen in pyridine derivatives (P) and the OH group in various carboxylic acids (A) was investigated by phase diagrams, X-ray studies and dielectric measurements. In mixtures with mono- and bifunctional pyridines respectively, increasing clearing temperatures and induced smectic A phases were found. Bifunctional nonliquid crystalline acids as components in mixtures with bifunctional pyridine derivatives give only compounds in the solid state. The data are interpreted by the formation of stable associate A_xP_y which acts as a new compound.

Keywords: hydrogen bridges, liquid crystals, phase induction, phase diagrams, X-ray studies, dielectric measurements

1. INTRODUCTION

An induction of liquid crystalline phases in binary systems can be observed relatively often.[1-6] This phenomenon can be explained by additional molecular interactions between different molecules.[7] One reason for the stabilization of the liquid crystalline state can be the intra- and intermolecular hydrogen bonds if they form disklike associates like dioles[8] or increase the length-to-breadth ratio of the rodlike molecules as observed in 4-subst.-benzoic acids[9,10] and trans-4-*n*-alkylcyclohexanecarboxylic acids.[11] Recently Kato *et al.*[12] and Pyzuk *et al.*[13] have shown the importance of the >N | . . . H—O—interaction for the stabilization of the liquid crystalline phase range in a binary system of the non liquid crystalline 4′,4-bipyridine and 4-*n*-butyl-benzoic acid and on cis-s-cis enaminoketones respectively. Especially in the first case, an induction of the smectic A modification and an increase of the nematic/isotropic transition temperature of about 30 K could be observed at a molar ratio pyridine:acid = 1:2. In order to get more information about the hydrogen bond between a pyridine derivative P and an carboxylic acid A phase diagrams of the following basic systems were investigated:

a)


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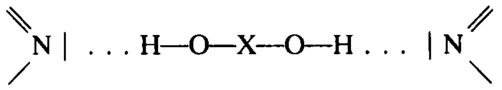
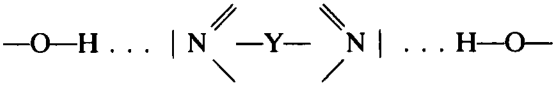
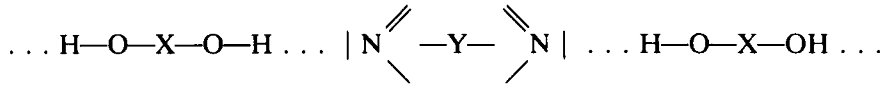
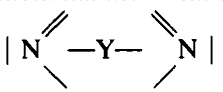


c)


d)


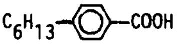
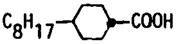
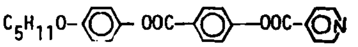
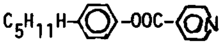
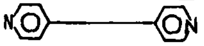
where  is a liquid crystalline pyridine, H—O— is a liquid crystalline carboxylic acid, H—O—X—O—H is a bifunctional acid with a different number of —CH$_2$— groups in the middle part, and  is the bifunctional bipyridine. X-ray and dielectric measurements were used for characterization of the assoziates.

2. SAMPLES AND EXPERIMENTS

The samples and the respective phase transition temperatures (in K) are given in Table I. It should be pointed out that with exception of the trans-4-*n*-octylcyclohexylcarbonic acid (OCA), all other samples exhibit only nematic (N) or no liquid crystalline phases (only solid (cr)/isotropic (is) transition). The pyridine derivatives

TABLE I

Phase transition temperatures in K

Sample		cr	S_B		N	is
HA		371	–	–		387
OCA		310		363		371
GA	HOOC-$(CH_2)_3$-COOH	369	–	–	–	–
PA	HOOC-$(CH_2)_5$-COOH	376	–	–	–	–
AA	HOOC-$(CH_2)_7$-COOH	379	–	–	–	–
BA	HOOC-$(CH_2)_{11}$-COOH	387	–	–	–	–
TP		397	–	–	–	411
DP		341	–	–	–	–
BP		384	–	–	–	–

were synthesized according to literature methods.[14,15] Three and two ring systems were taken in order to study the influence of molecular geometry on the stability of the associates. BP was purchased from Merck Schuchardt.

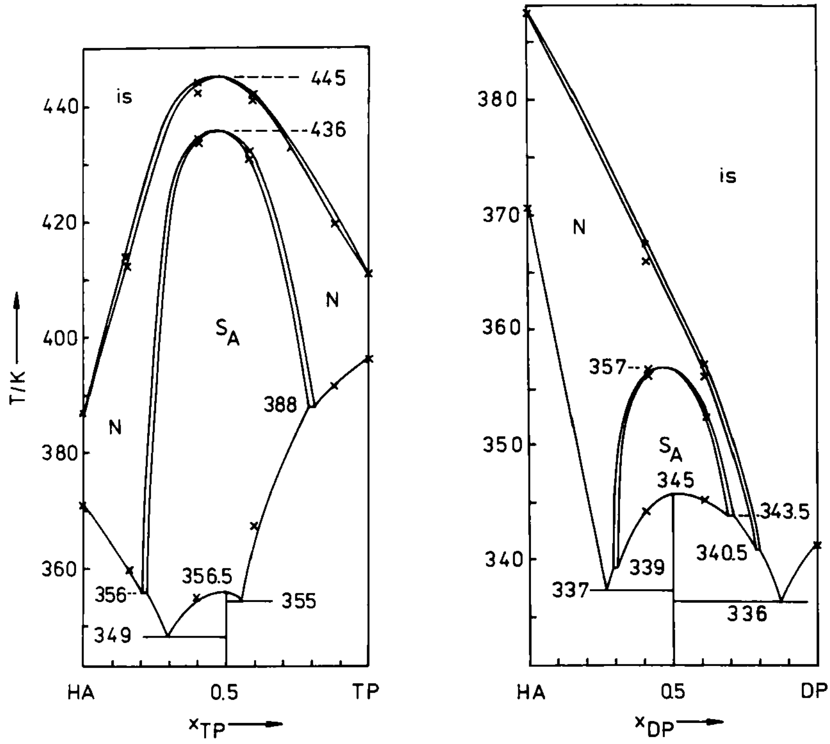
Phase diagrams are investigated by a heating stage microscope using the contact method[16] and single concentrations. Because of a strong tendency of DP to sublimate the phase diagrams involving this compound were mainly determined by the contact method.

X-ray studies are performed using magnetically oriented samples. The scattered intensity has been recorded with a flat film.

Dielectric measurements are carried out in the frequency range from 1 kHz to 100 kHz on oriented samples. The measuring cell flat electrodes had area of about 2 cm^2 and were separated by 0.2 mm.

3. RESULTS

Phase diagrams of the two (DP) and three (TP) ring pyridine compounds with 4-n-hexylbenzoic acid are given in Figures 1 and 2. Typically all diagrams show the induction of a smectic A modification, and formation of a compound AP in the

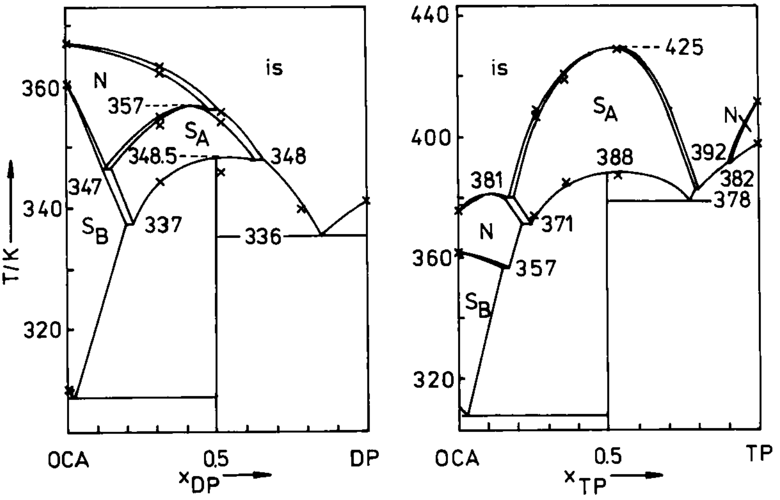


FIGURES 1 and 2 Phase diagrams of 4-*n*-hexylbenzoic acid (HA) with a three (TP) and two (DP) ring pyridine. Three phase reactions, eutectica and maxima were detected by the contact method. This temperatures (T/K) are given in the phase diagram. Phase transition temperatures found by single concentrations are indicated by *X*.

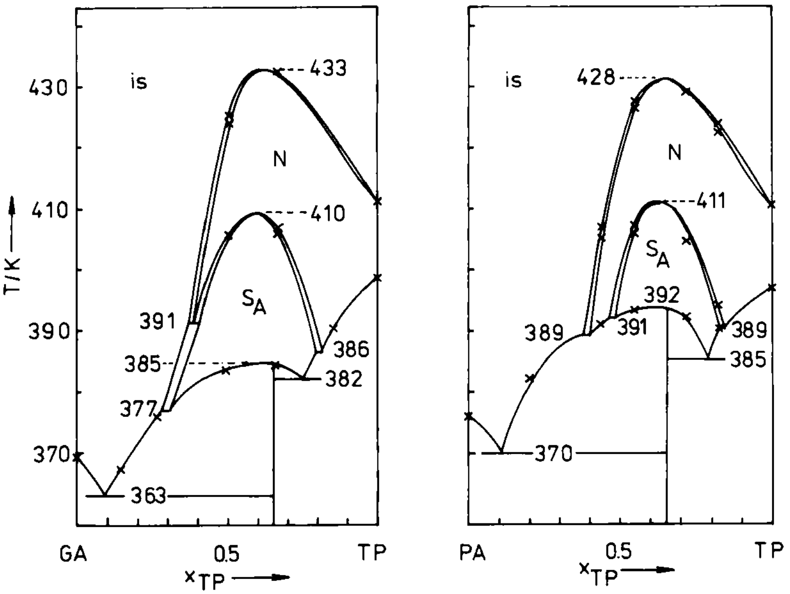
solid state indicated by two eutectic temperatures. In the phase diagram in Figure 1 the stability of nematic phases at $x_{TP} = 0.5$ increases by 46 K with respect to the expected value from the additivity of the clearing temperatures of the pure compounds. Additionally the induced S_A phase is observed up to 436 K. Obviously the interaction between HA and TP results in a new chemical compound[12] with a smectic A/nematic polymorphism, and a higher clearing temperature than as both single compounds HA and TP, respectively. Contrary to this result, the mixture of 4-*n*-hexylbenzoic acid with DP does not show any increase of the clearing temperature with increasing concentration of DP (Figure 2). However, the induced smectic A phase is again detected in the middle of concentration range, without tendency to form a maximum in the clearing temperature.

In the binary systems with trans-4-*n*-octylcyclohexylcarboxylic acid (OCA) the relatively high ordered smectic B phase is destroyed by addition of the pyridine derivatives and a less ordered smectic A phase is induced in the middle concentration range (Figures 3 and 4). The general difference between both diagrams is again that the shorter DP is unable to stabilize the liquid crystalline state in such a way that a maximum in the clearing temperature can be found. The associate compound of the type AP which is clearly detected in the solid state has only a smectic A phase and a clearing temperature of about 357 K, whereas AP with the longer TP shows a clearing temperature of about 425 K. Therefore, we conclude that the molecular length of the pyridine component is important for the stability of the liquid crystalline state of the intermediate compound AP, at least at low temperatures at which the $\rangle$N | . . . H—O—bond is stable.

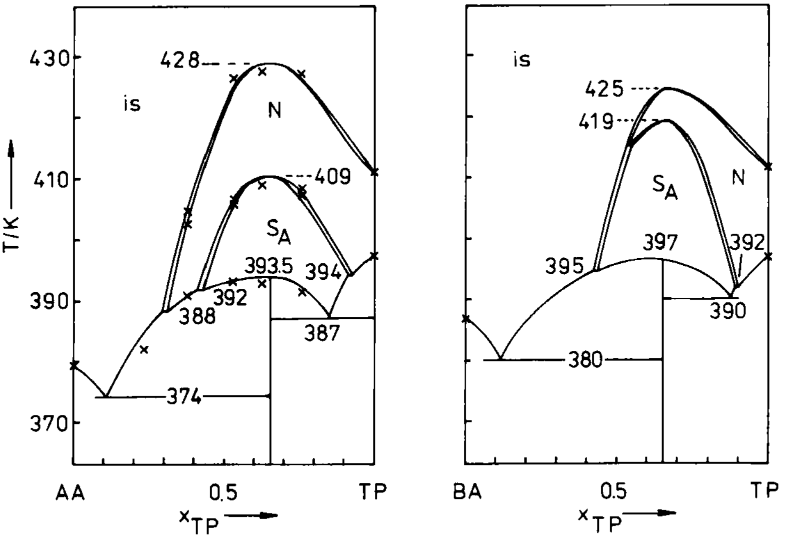
As shown in the Figures 5–8, nonmesogenic bifunctional acids (i) visibly increase the clearing temperatures by about 20 K with respect to that of 4-*n*-hexylbenzoic acid (HA), (ii) induce a smectic A phase, and (iii) form a solid compound of the



FIGURES 3 and 4 Phase diagrams of trans-4-*n*-octylcyclohexylcarbonic acid OCA with the two and three ring pyridine.



FIGURES 5 and 6 Phase behaviour of the bifunctional acids GA and PA containing three and fifc CH_2-groups respectively with the three ring pyridine. All maxima arises at x_{TP} = 0.66.



FIGURES 7 and 8 Phase diagrams of the bifunctional acids with seven (AA) and eleven (BA) CH_2-groups.

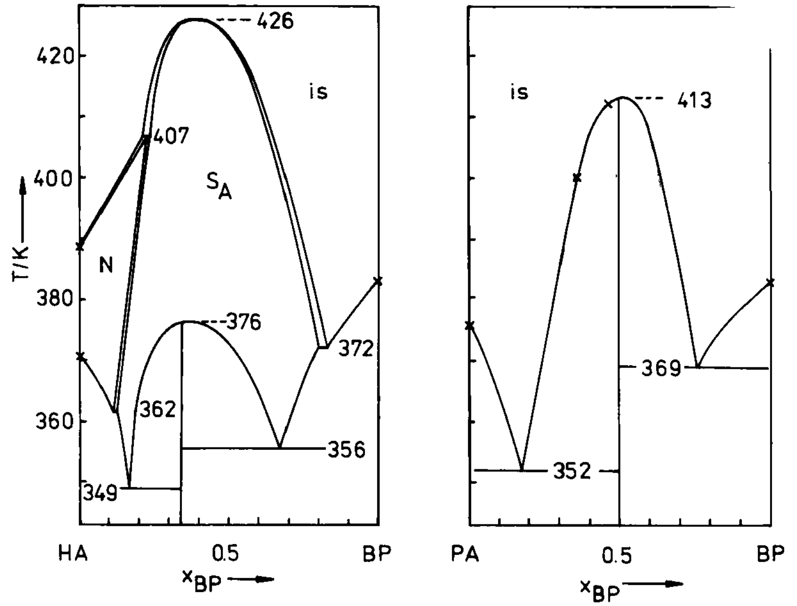
type AP_2. Contrary to Figures 1–4 where maxima of stability are at about x = 0.5 two pyridines and one bifunctional acid form an associate which is stable for x(Pyridine) = 0.6 up to 430 K. Increase of the number of CH_2-groups in the acids from 3 to 11 results only in a small decrease of the clearing temperature maximum from 433 K to 425 K. The acid has here the function of a linkage between two liquid crystalline units and in this way increases the order in the system. This can be seen in variation of the maximum of the S_A/N transitions which increase from 410 K (GA) to 419 K (BA).

The phase diagram of the bifunctional bipyridine BP with 4-*n*-hexylbenzoic acid HA in Figure 9 is mainly investigated by the contact method, because of a strong tendency for sublimation of BP. The results are in agreement with the former with one difference: the compound A_2P is formed now in the solid state as well as in the smectic A and nematic modifications.

In the phase diagram of the bifunctional acid PA and bipyridine no liquid crystalline phase could be detected. As shown in Figure 10, only in the solid state a compound of the AP type exist. This again confirms that the nonliquid crystalline bifunctional compound acts only as a link, and stabilizes in this way the respective phases. The linkage and liquid crystal form a common associate of the type A_xP_y which can be regarded as a new compound miscible with the high temperature phase of the respective liquid crystal.

The formation of associates in direction of the long molecular axes should influence the thickness of the smectic layers (d). Two X-ray preliminary experiments with the systems HA/BP $x_{BP} = 0.3$ (Figure 9), and GA/TP $x_{TP} = 0.6$ (Figure 7) showed X-ray patterns characteristic for the structure of the S_A phase. The d-values of in the S_A phase exceeded considerable molecular dimensions (molecular lengths are $L_{GA} = 1.12$ nm, $L_{TP} = 2.56$ nm, $L_{HA} = 1.6$ nm and $L_{BP} = 1.2$ nm). It has been found that

$$d_{0.3} = 3.65 \text{ nm for } x_{BP} = 0.3 \quad \text{and} \quad d_{0.6} = 5.8 \text{ nm for } x_{TP} = 0.6.$$



FIGURES 9 and 10 Phase diagram between 4-*n*-hexylbenzoic acid HA and the bifunctional bipyridine BP investigated by the contact method. In the diagram between the bifunctional acid PA and BP the highest melting temperature of the associate and no liquid crystalline phase were detected.

Although the intermolecular structure of the associates is unknown, one can guess a possible correlation between the experimental d-values and molecular lengths

$$d_{0.3} = 2 \times L_{HA} + 1 \times L_{BP} \, (=4{,}4 \text{ nm})$$

$$d_{0.6} = 1 \times L_{GA} + 2 \times L_{TP} \, (=6.2 \text{ nm})$$

where we assumed that the intermolecular association has a form of a fully extended train of component molecules. The agreement between experimental and anticipated d-values seems to support such a form of association. Dielectric measurements were carried out on TP and a equimolar mixture of TP and HB. The three ring pyridine derivative has a static dielectric anisotropy of $\Delta\varepsilon(\text{TP}) = 0.03$ at $T = 0.98\ T_{N/is}$. Since the equimolar mixture has had a high conductivity, the error of measured was substantial $\Delta\varepsilon(\text{TP, HB}) = 0.27 \pm 0.03$. The dielectric anisotropy of HA is $\Delta\varepsilon$ (HA) = 0.30.[17] Following the simple mixing rule, the dielectric anisotropy of $0.5 \times 0.30 + 0.5 \times 0.30 = 0.165$ can be expected. The much higher experimental value of $\Delta\varepsilon$(TP, HB) indicates formation of an associate with a bigger longitudinal dipole moment, due to a destruction of the symmetrically dimer acid. Generally, it can be concluded that the associate between the acid A and pyridine P has the character of a stable intermediate compound. At temperatures of about 440 K a dissociation into its two or three components occurs.

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