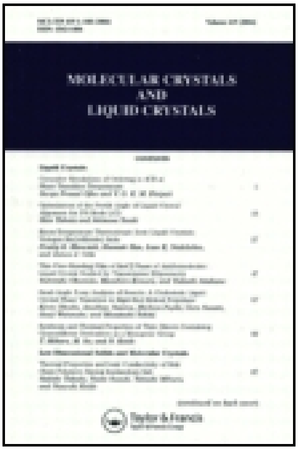

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Stabilization and Destabilization of Liquid Crystalline Phases by Hydrogen Bondings

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Stabilization and Destabilization of Liquid Crystalline Phases by Hydrogen Bondings

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Stabilization and destabilization of liquid crystalline phases in mixtures of derivatives of phenol and cyclohexanole with pyrrolidines and pyridines were investigated by phase diagrams. Whereas in mixtures with pyrrolidines a strong destabilization of the liquid crystalline state was found, mixtures with pyridines stabilize LC phases. The results are interpreted by 1:1 associates formed by hydrogen bridges and the molecular shape of these complexes.

Keywords: Phenols, pyrrolidines, pyridines, hydrogen bridges, phase diagrams, LC-phase, stabilization, destabilization.

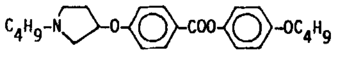
1. INTRODUCTION

Recently Kato, Frechet *et al.*[1–4] and Griffin and his coworkers[5] reported a stabilization of nematic and smectic A liquid crystalline phases by hydrogen bondings in binary systems of derivatives of benzoic acids *E* and pyridines P. Kresse *et al.*[6] extended these investigations to derivatives of trans-4-*n*-cyclohexanecarboxylic acids and ω-dicarboxylic acids. In all known experiments the existence of the associates PE, PE_2 and P_2E is shown by a maximum in the melting curves at the respective molar fraction x in the phase diagrams.[5,6] Furthermore X-ray[4,5,6] spectroscopic[2,3] and dielectric[6] measurements were carried out.

The hydrogen bonding shows the highest stability if the proton donator A—H is linearly arranged with the free electron pair of the acceptor A—H···IN.[7] In this way hydrogen bridges can stabilize the mesomorphic state. In order to test new proton donators phase diagrams of derivatives of pyrrolidine Py and pyridine P with two different phenols F1 and F2 and a cyclohexanol F3 were investigated by the contact method[8] and single concentrations, using a heating stage microscope. We were especially interested in the solid/liquid transition at the molar fraction $x = 0.5$ which should indicate the formation of a solid compound PF by a maximum.

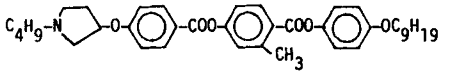
2. SAMPLES AND PHASE DIAGRAMS

First, phase diagram of 4-*n*-butyloxyphenyl 4-(1-*n*-butylpyrrolidine-3-yloxy)benzoate and 4-*n*-nonyloxyphenyl 4-[4-(1-*n*-butylpyrrolidine-3-yloxy)]benzoyloxy-2-methylbenzoate were investigated. It is of interest that the extension of 4-*n*-butyloxyphenyl



Py1

cr 344 N 352 is (temperatures in K)



Py2

cr 365 N 406.5 is

4-*n*-butyloxybenzoate (cr 355 N 365 is[9]) by the pyrrolidine group results in a decrease in the clearing temperature of 13 K. This effect should be mainly caused by the pyramidal structure of the IN unity where the butyl group partially acts like a lateral substitution. On the other hand this group is able to form hydrogen bridges using the

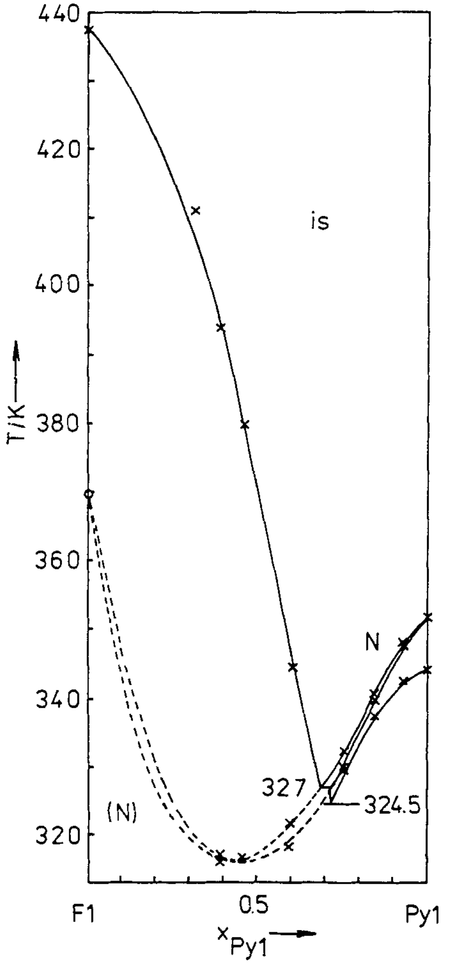
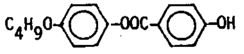


FIGURE 1 Phase diagram of 4-*n*-butyloxyphenyl 4-(1-*n*-butylpyrrolidine-3-yloxy)benzoate Py1 with 4-*n*-butyloxyphenyl 4-hydroxybenzoate F1. Transition temperatures (contact method) are directly given in the diagram, single concentrations are indicated by x.

free electron pair and will be transformed in a tetrahedral structure. Phase diagrams of the given pyrrolidines with 4-*n*-butyloxyphenyl 4-hydroxbenzoate are shown in



F1

cr (369.5 N) 437 is

Figures 1 and 2. The monotropic clearing temperature of *F1* was extrapolated from phase diagrams with nematic samples without special interactions.

In the diagrams a minimum of the clearing temperature could be detected, indicating a destabilization of the nematic phase. Obviously the formation of the associate is connected with a reduction of the length-to-breath ratio in relation to that of the starting compounds. The hydrogen bonded part can be regarded as a lateral branch. The liquids curve does not give a hint of the formation of a solid compound PyF.

The replacement of the pyrrolidines by 4(4-*n*-pentyloxyphenyloxycarbonyl)phenyl-pyridine-4-carboxylate results in a maximum of the liquidus curve at equimolar

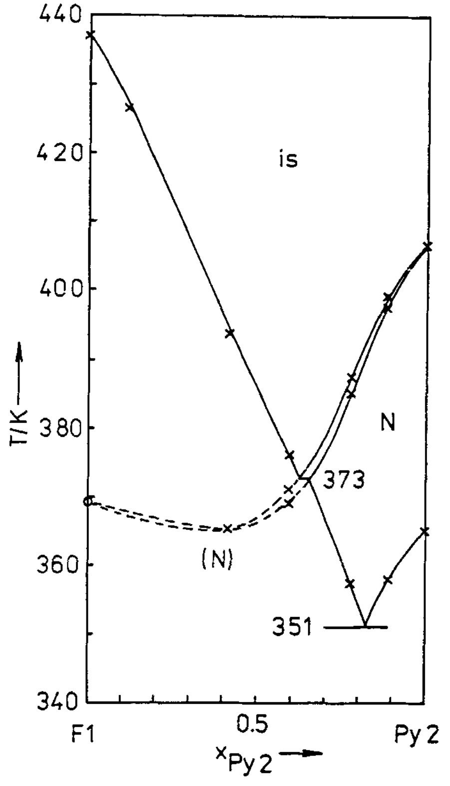


FIGURE 2 Binary system of 4-*n*-nonyloxyphenyl 4-[4-(1-*n*-butylpyrrolidine-3-yloxy)]benzoyloxy-2-methylbenzoate Py2 with 4-*n*-butyloxyphenyl 4-hydroxybenzoate F1.

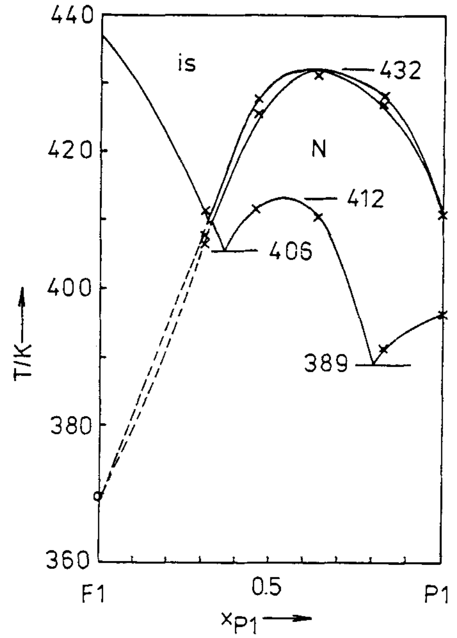
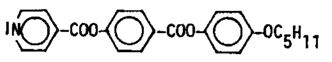


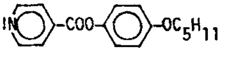
FIGURE 3 Phase diagram of 4(4-*n*-pentyloxyphenyloxcarbonyl)phenyl pyridine-4-carboxylate P1 and 4-*n*-butyloxyphenyl 4-hydroxybenzoate F1. The 1:1 associate P2F1 can be detected by the maximum of the liquidus curve at 432 K.

concentration and a strong stabilization of the nematic phase N indicated by a maximum of the clearing temperature as shown in Figure 3. If the three ring compounds P1 is substituted by the two ring 4-*n*-pentyloxphenyl pyridine-4-carboxylate no induced liquid crystalline phase could be detected. An eutecticum at 336 K on the side of P2 and a peritecticum of P2F1 at 388 K were found by the contact method.



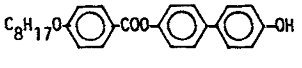
P1

cr 397 N 411 is



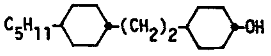
(cr 341 is) P2

An elongation of the associate can be obtained if F1 is replaced bv 4-(4′-hydroxy)biphenyl 4-*n*-octyloxybenzoate as shown in the phase diagram with 4(4-*n*-heptyloxyphenyloxycarbonyl)phenylpyridine-4-carboxylate which exhibit nearly the same transition temperatures as P1 (Figure 4).



F2

cr 453 N 493 is



(cr 445 is) F3

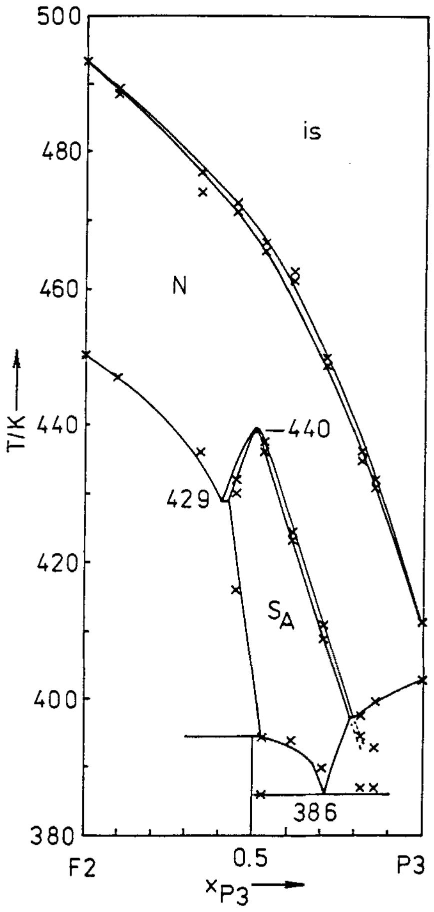
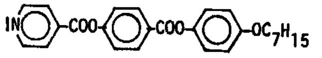


FIGURE 4 Phase behaviour of the mixture 4(4-*n*-heptyloxyphenyloxycarbonyl)phenyl pyridine-4-carboxylate P3 and 4-(4-hydroxy)biphenyl 4-*n*-octyloxybenzoate F2.

The peritecticum of P3F2 at 395 K indicates the formation of a 1:1 compound which has a smectic A and a nematic phase.

A less acidic hydroxy group exists in the aliphatic trans-4[2(trans-4-*n*-pentylcyclohexyl)ethyl] cyclohexanol



P3

cr 403 N 411 is

In the mixture with P1 in Figure 5 a the stabilization of the nematic phase and an induction of the smectic A state can be observed. The stability of the liquid crystalline phase is nearly the same as found in the mixture with the two ring phenole in Figure 3. A stable solid compound P1F3 could also be detected. This again is evidence that cyclohexanols can form very stable hydrogen bondings.[11]

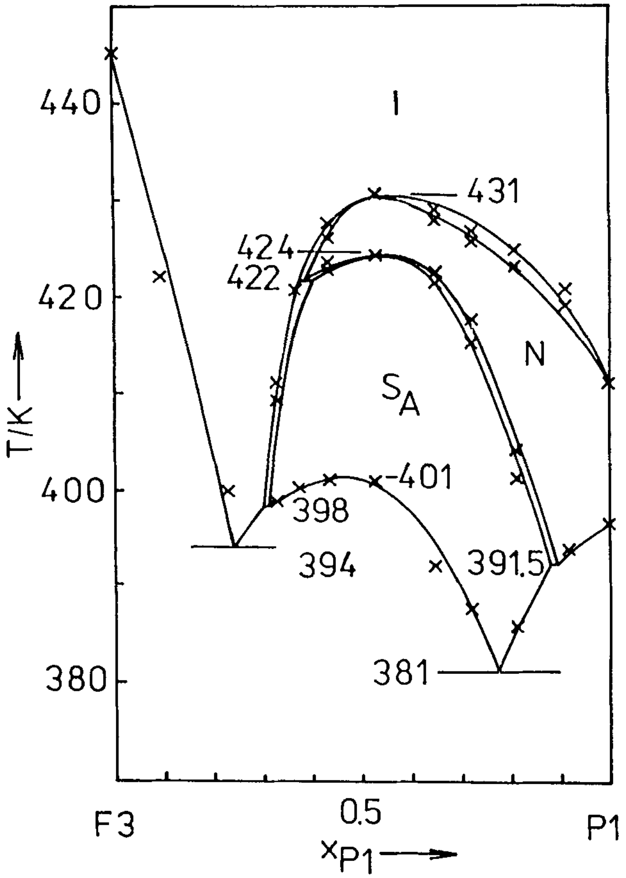


FIGURE 5 Binary system of 4(4-*n*-pentyloxyphenyloxycarbon)phenyl pyridine-4-carboxylate P1 and trans-4-[2-trans-4-*n*-pentylcyclohexyl)ethyl]cyclohexanol F3.

It should be pointed out that alkyldiols, which are ordered in bilayers, do not associate with pyridines in the solid state or stabilize liquid crystalline phases. The miscibility with *P1* is restricted in this case to the concentrations near to the pure compounds.

3. CONCLUSIONS

Derivatives of phenole and cyclohexanole from 1:1 associates by hydrogen bondings with pyridines as shown in the melting curves of phase diagrams. Due to the extension of the length-to-breath ratio of the molecular units the clearing temperature of the associates increases and smectic A phases are induced. On the other hand, hydrogen bridges can act as a lateral substitution and destroy the liquid crystalline state as shown in systems with pyrrolidines.

References

1. T. Kato and J. M. J. Fréchet, *Macromolecules*, **22**, 3818 (1989).
2. T. Kato and J. M. J. Fréchet, *Am. Chem. Soc.*, **111**, 8533 (1989).
3. T. Kato and P. G. Wilson, A. Fujishima and J. M. J. Fréchet, *Chem. Lett.*, (*Japan*) **1990**, 2003.
4. U. Kumer, T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **114**, 6630 (1992).
5. C. Alexander, C. P. Jariwala, C. M. Lee, C. R. Walton and A. C. Griffin, "Hydrogen bonded pyridine-carboxylic acid mesogens", 14th International LC Conference, June 21–26, 1992 Pisa, Italy, abstracts AIL1, P. 6.
6. H. Kresse, I. Szulzewski, S. Diele and R. Paschke, *Mol. Cryst. Liq. Cryst.* **238**, 13 (1994).
7. G. Geisler and H. Seidel, Die Wasserstoffbrückenbindung, WTB Chemie, Akademieverlag Berlin 1977, pp. 125–138.
8. L. Kofler and A. Kofler, Thermo-Mikro-Methoden zur Kenntnis organischer Stoffe und Stoffgemische, Verlag Chemie Weinheim, 1954.
9. D. Demus, H. Demus and H. Zaschke, Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1974, p. 67.
10. I. Szulzewski, *Diplomarbeit*, Halle 1992.
11. A. G. Michell and H. G. Higgins, *Tetrahedron*, **21**, 1109 (1965).