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Hydrogen-Bond Induced Liquid Crystalline Phases in Compounds with a Carbonyl Group as Proton Acceptor

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Binary systems of ketones and aldehydes as proton acceptors with different donors were investigated. The existence of different hydrogen bonded liquid crystalline associates was proven by the induction of the smectic A phase as well as by IR-spectroscopic measurements.

Keywords: Liquid crystals; phase induction; hydrogen bond; ketones; aldehydes

1. INTRODUCTION

It is well known that liquid crystalline phases can be obtained by self-organization processes of samples with proton donors D and respective acceptors A. Donor–acceptor combinations which were intensively investigated in the past are derivatives of benzoic acids with substituted pyridines. Such systems were introduced at first by Kato and co-workers [1]. Later the investigations were extended to obtain associates with different phases or molecules with different molecular shape [2–16]. Recently Bernhardt *et al.* published a rule how different liquid crystalline associates

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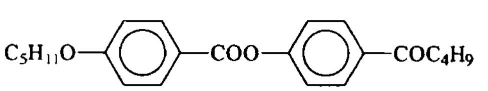
can be designed [17]. The general idea given by the authors is based on the mesophase stability as function of the acidity of the donor. Using this idea we produced smectic B phases in systems where the pure components do not exhibit liquid crystalline phases themselves. In the same way also associates with smectic E phases were obtained [18, 19].

Derivatives of phenol were used only in few examples as donors [8, 11, 20, 21]. The problem to introduce new donors or acceptors is the stability of the associates DA relatively to that of D and A. Especially, one has to consider that the proton donor also forms homomolecular hydrogen bonded associates which have to be destroyed in order to form DA. Furthermore, one has to take into account the geometrical shape of the associate which can stronger deviate from the classical rod-like molecular shape (see for example [11, 15, 16]). Under this circumstances the classical system benzoic acid/pyridine seems to be well suited.

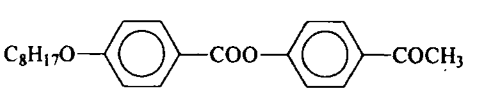
Nevertheless, we tried to enlarge the number of functional groups which can form stable liquid crystalline associates. In this contribution we report about our attempts using the —CO— group as proton acceptor functions.

2. KETONES AS ACCEPTOR COMPONENTS

For our experiments we choose two ketones which exhibit a liquid crystalline phase [22, 23] themselves. Thus, it is also possible to study the destruction of the liquid crystalline phases by formation of associates.



cr 349 S_A 386 I **A1**



cr 357 S_A 368 I **A2**

Firstly, 4-*n*-hexylbenzoic acid **D1** (cr 371 N 387 I) and 4-*n*-hexyloxyphenylacetic acid **D2** (cr 352 I) were mixed with **A1**. Thereby all phase transition temperatures are given in K. In all cases the binary phase diagrams were investigated by contact method [24] and partially also using single concentrations by means of a polarizing microscope (JENAPOL) in combination with a heating stage (LINKAM). The phase diagram in Figure 1 shows a destabilization of the S_A-phase and decreasing clearing temperatures in the middle concentration range. Three reasons can be considered for this effect:

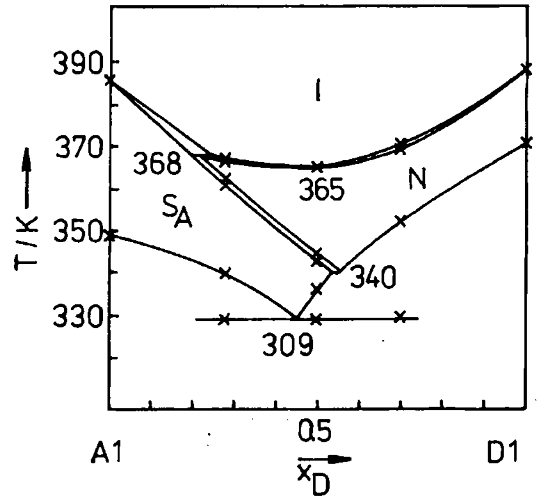


FIGURE 1 Phase diagram of **A1** and 4-*n*-hexylbenzoic acid **D1**. The temperatures detected by contact method are given as numbers, results on single concentrations are indicated by crosses.

i) the angular shape of the associated molecule **A1D1**,

ii) the long lateral substituent (butyl group) of the associate (see the sketch in Fig. 3). The influence of such laterally attached long-chain group reduces the mesophase stability [25],

iii) no strong hydrogen bond [17].

Using **D2** a second angular segment was inserted, but – as demonstrated in Figure 2 – without success. Probably, a rod-like associate could not be obtained due to the rotation of **D2** around the hydrogen bond and of the CH_2-group of the substituted phenylacetic acid. A shortening of the lateral group can be obtained using the acetyl substituted compound **A2** as proton acceptor. The phase diagrams with **D1** and 4-*n*-heptyloxybenzoic acid **D3** (cr 366 S_C 371 N 420 I) shown in Figures 4 and 5 indicate the destabilization of the S_A-phase. Comparing the phase diagrams in Figures 1 and 4 it can be established that the destabilization of the liquid crystalline phases in the system with **A2** is lower. Furthermore, for the binary system in Figure 5a small stabilization of the S_A-phase occurs. This indicates the influence of the length of the lateral alkyl group in the associates.

From earlier experiments it is known that the S_A-phase becomes stabilized in associates of α,ω-dicarboxylic acids and pyridines [7]. Therefore, 1,10-decanedicarboxylic acid **D4** (cr 408–410 I) and perfluoro-1,10-decanedicarboxylic acid **D5** (cr 424–433 I) were mixed with **A2**. The respective phase diagrams are given in Figures 6 and 7. One can recognize that only

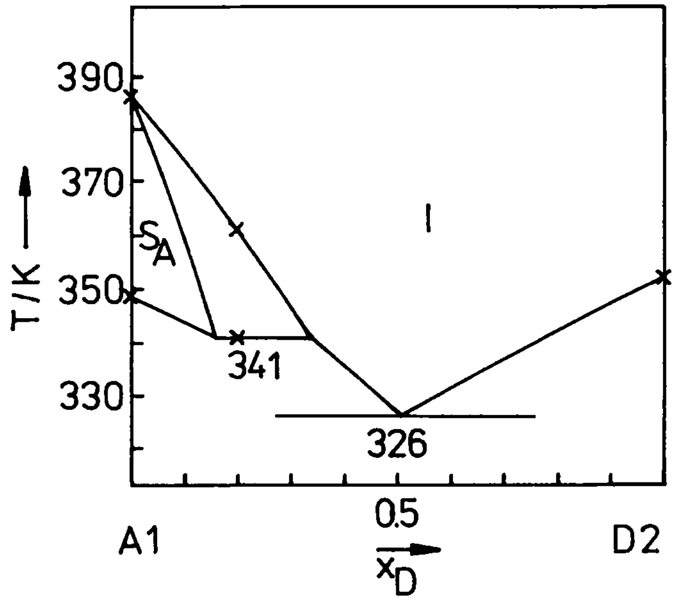


FIGURE 2 Binary system of ketone **A1** and 4-*n*-hexyloxyphenylacetic acid **D2**.

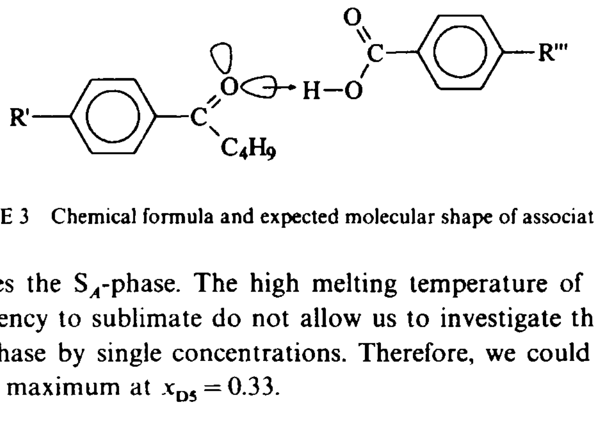
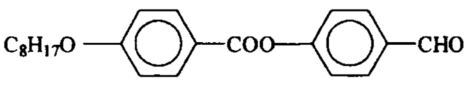


FIGURE 3 Chemical formula and expected molecular shape of associate **A**i**D1**.

D5 stabilizes the S_A-phase. The high melting temperature of **D5** and the strong tendency to sublimate do not allow us to investigate the maximum of the S_A-phase by single concentrations. Therefore, we could not exactly confirm the maximum at $x_{D5} = 0.33$.

3. ALDEHYDE AS ACCEPTOR COMPONENTS

A further possibility to reduce the influence of the lateral alkyl group resulting from the ketones is its substitution by a hydrogen atom [26]:



cr_{II} 317 cr_I 330 N 340 I **A3**

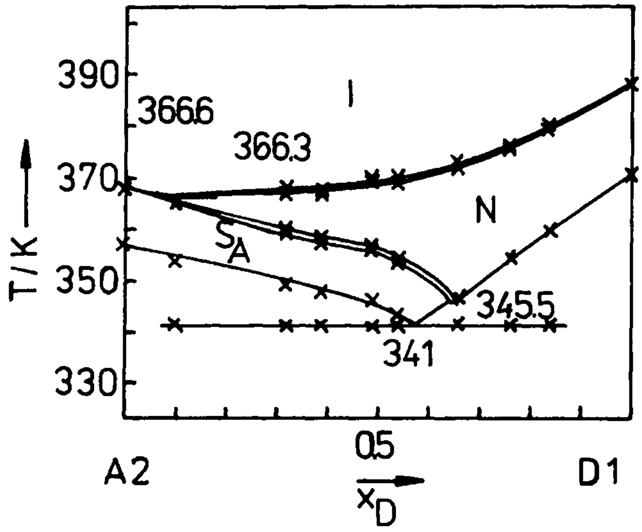


FIGURE 4 System **A2** and 4-*n*-hexylbenzoic acid **D1**. The temperatures 366.3 K and 366.6 K are related to the minimum of the N/I curve and to the three phase reaction S_A/N/I, respectively.

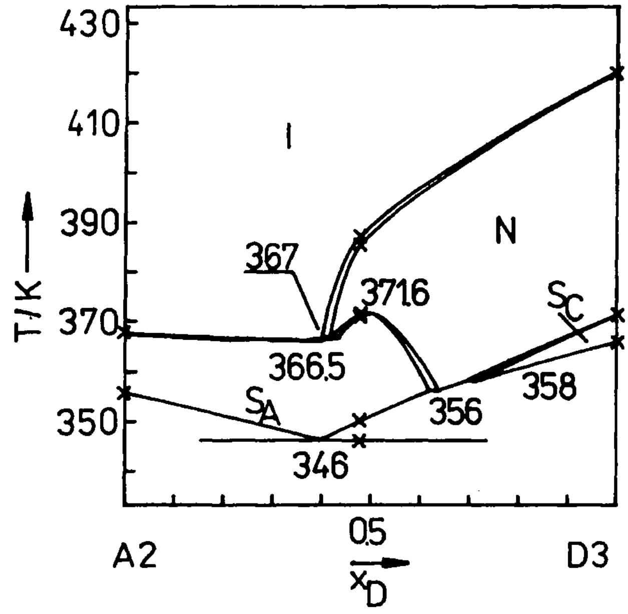


FIGURE 5 Phase diagram **A2**/4-*n*-heptyloxybenzoic acid **D3**.

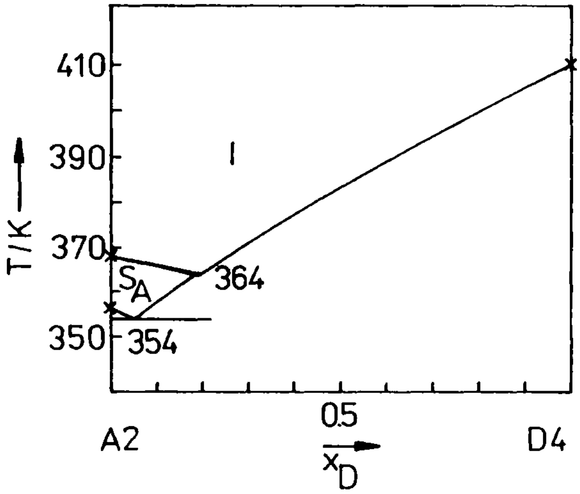


FIGURE 6 Binary system **A2**/1, 10-decanedicarboxylic acid **D4**.

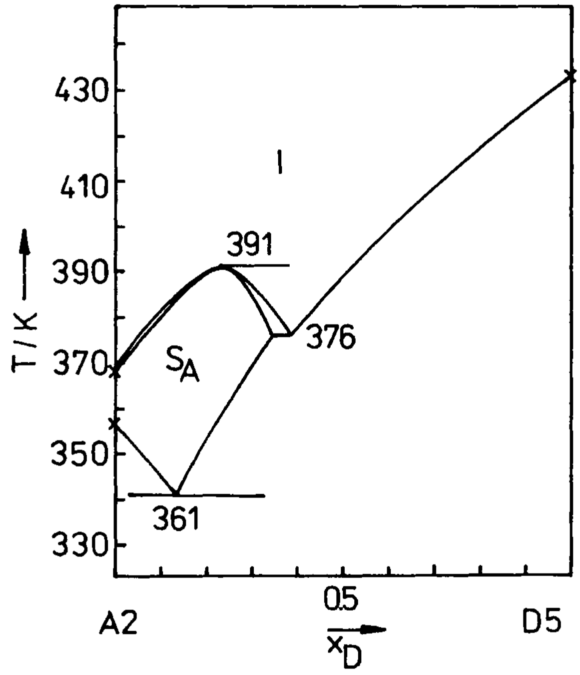


FIGURE 7 Binary mixture **A2**/perfluoro-1, 10-decanedicarboxylic acid **D5**.

In this case we were interested on low phase transition temperatures to avoid decomposition or oxidation of the acceptor. Phase diagrams of **A3** with **D1** and trans-4-*n*-octylcyclohexane-carboxylic acid **D6** (cr 310 S_B 361 N 371I) in the Figures 8 and 9 give a nearly linear relation between the clearing temperatures of the components and the induction of a S_A-phase in the middle concentration range. This can be considered as a hint for the formation of 1:1 associates. The two eutectic temperatures at 309 and 301 K in Figure 10 are related to the two solid modifications of **A3**. Smectic A phases are also induced in the binary mixtures of the formyl derivative **A3** with **D3** (Fig. 10). Surprisingly, a S_A-phase is detected in the supercooled range of the phase diagram with 4-*n*-nonyloxyphenol **D7** (cr 341–342 I) shown in Figure 11. In this case the S_A-state is less stable in comparison with that of Figure 10. In contrast to Figure 10, a destabilization of the liquid crystalline state recognizable by the lowering of the clearing temperatures is detected. The addition of α,ω-dicarboxylic acids results in different behavior (Figs. 12 and 13). Whereas for the nonfluorinated acid **D4** a "slight" destabilization of the liquid crystalline state takes place, we could find a small stabilization of the nematic phase for the perfluorinated **D5**.

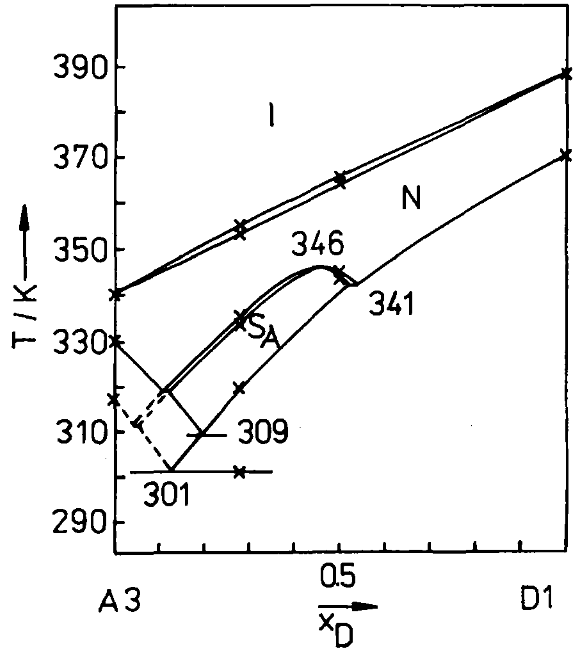


FIGURE 8 Phase diagram of **A3** with 4-*n*-hexylbenzoic acid **D1**.

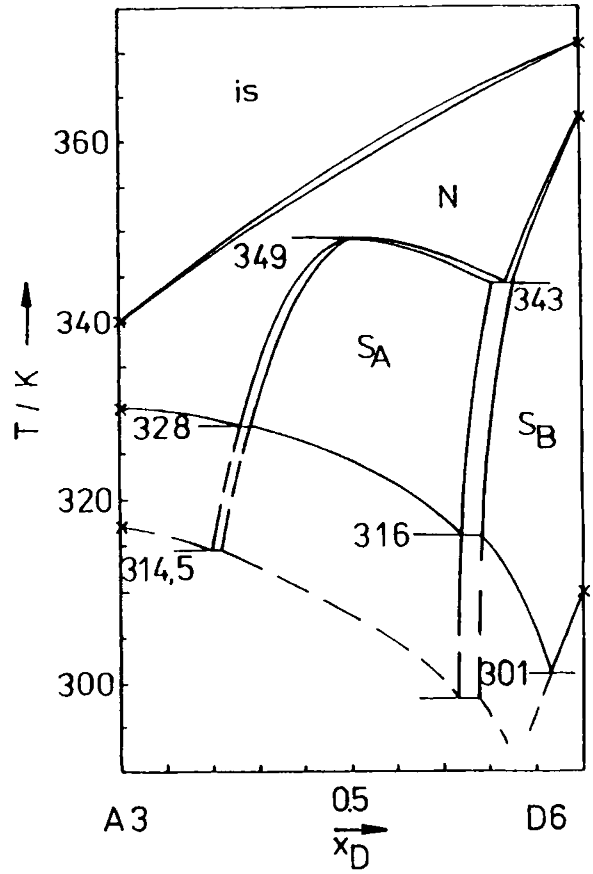
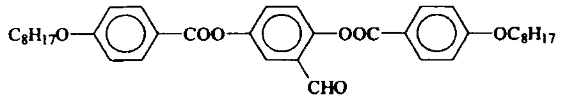


FIGURE 9 Binary mixture of **A3** with trans-4-*n*-octylcyclohexane carboxylic acid **D6**.

The high melting temperature of **D5** obstruct the detection of the maximum in the nematic state.

In a further experiment we tried to achieve a liquid crystalline associate between a laterally attached acceptor function and the proton donor. For this purpose the aldehyde **A4** [27] was mixed with donor **D6**. As seen in the phase diagram in Figure 14 neither an induction of a S_A-phase nor a maximum in the N/I transition curve were found.



cr. 358 N 429 I

A4

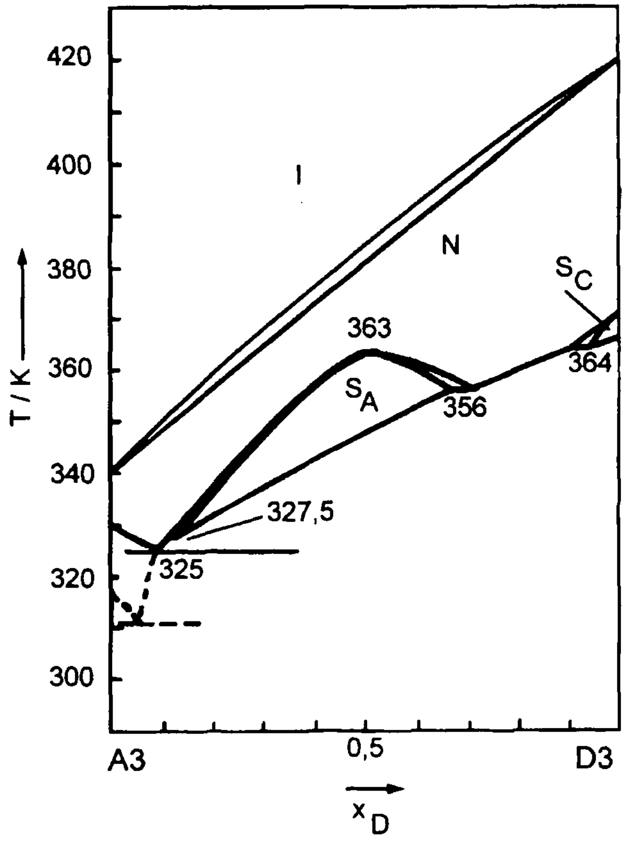


FIGURE 10 System of A3 and 4-*n*-heptyoxybencoic acid D3.

4. IR-SPECTROSCOPIC INVESTIGATIONS

The existence of two eutectic points in a phase diagram is a clear thermodynamical indication for the formation of a stable associate in the solid state (see for example [7, 8]). Such associates can differ in the polymorphism of the solid and mesomorphic state from that of the pure donor and acceptor. It is obvious that in mixtures of carboxylic acids and pyridines [7] and [8] the associates are formed by hydrogen bonds. On the other hand there is no reason that such singular associates will be destroyed at the melting point. So, it could be found by X-ray measurements that the layer thickness agrees well with the length of the associated molecules and not with that of D_2 or A [7].

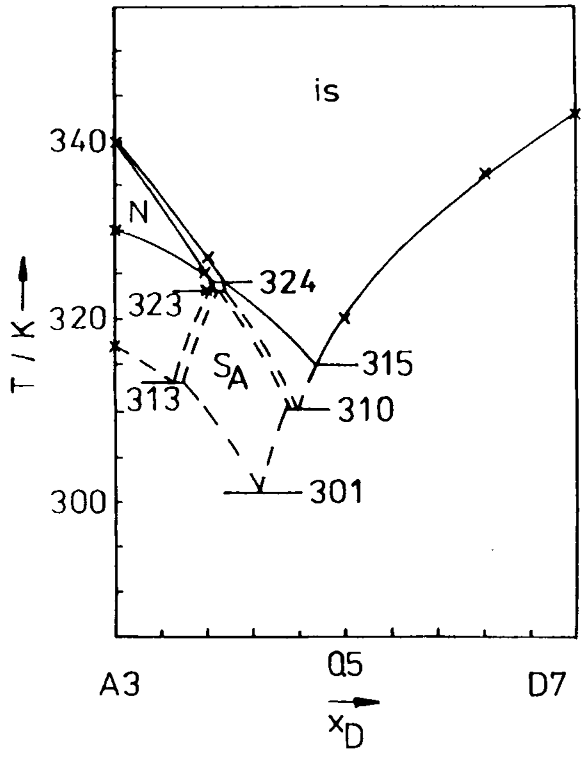


FIGURE 11 Phase diagram of **A3** and 4-*n*-nonyloxyphenol **D7**.

Such a thermodynamical evidence can not be given for the phase diagrams in this paper. Therefore, we can not conclude on the species and strength of the hydrogen bonds formed in the binary systems, specially on homeomolecular D_2 and heteromolecular DA associates. To prove the existence of heteromolecular associates in compounds with carbonyl groups we performed infrared measurements of the mixtures **D1/A3** and **D1/A1** with $x_{D1} = 0.45$ and 0.5, respectively using a FT-IR spectrometer (IFS 25, Bruker).

The spectra of the pure carboxylic acid **D1** and of the aldehyde **A3** at one temperature as well as of the associate at different temperatures are shown in Figure 15. The carboxylic function of **A3** exhibits an intense and broad CO absorption at 1695 cm^{-1} which is characteristic for the hydrogen bonded CO species in homomolecular associates of formyl compounds. Additionally, we found a signal at 1735 cm^{-1} at all temperatures which is

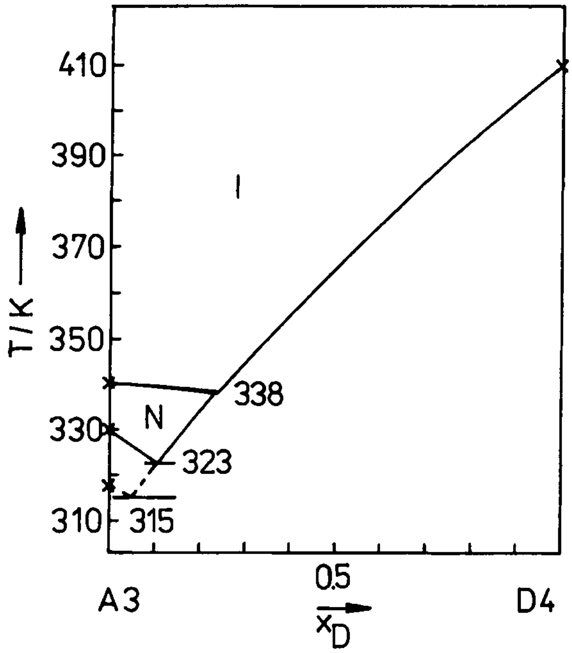


FIGURE 12 Mixture of **A3** and 1, 10-decanedicarboxylic acid **D4**.

due to a non-associated carbonyl function (Fig. 15a). The COH deformation bands in the spectral region between 1000 and 800 cm^{-1} can be considered as a sensitive indicator for changes in the dimeric associates [28]. In this region the maximum of the signal at 951 cm^{-1} is shifted to lower wavenumbers by about 25 cm^{-1} with increasing temperature (Fig. 15b).

Thus, due to the increasing mobility of the molecules the strength of the hydrogen bond is lowered. At temperatures above the N/I phase transition we did not observe significant changes of the position of the signals mentioned above compared to those in the liquid crystalline phase. Thus, we conclude that the associates formed in the liquid crystalline phase are of the same nature like those in the isotropic phase. The spectrum of the pure acceptor compound **A3** does not show any temperature induced changes of signals in the relevant region of the CO stretching and COH deformation vibrations.

In contrast to the spectrum of the pure carboxylic acid, an intense CO stretching vibration was observed at 1737 cm^{-1} in all phases of the mixture **D1/A3** with $x_{D1} = 0.45$. Thus, in the heteromolecular system the formed

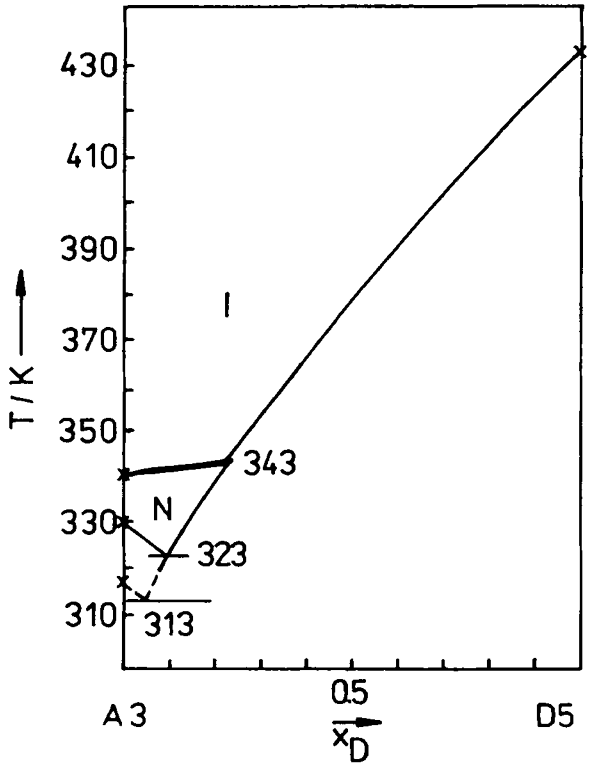


FIGURE 13 Binary system of **A3** and perfluoro-1, 10-decanedicarboxylic acid **D5**.

associates are less stable than in the pure acid. From the CO stretching region it cannot be decided if the formed associates are heteromolecular in the mixtures or if only a dilution of the acid associates take place. Therefore, the COH deformation region was considered. In the smectic A phase (at 343 K) a broad asymmetric band with a maximum at 940 cm^{-1} and a shoulder was observed indicating the coexistence of different COH species. If we compare the spectra of the mixture with that of the pure acid we found the maximum of the associate band shifted to lower wavenumbers. Therefore, we have to consider that different associated species like **A3A3** and **D1A3** can exist. With increasing temperature the associate signal at 940 cm^{-1} decreases and the aldehyde band at about 970 cm^{-1} increases. Therefore, the aldehyde associates break apart significantly. Caused by the broadness of this band we cannot exclude the acid-acid associates, but from

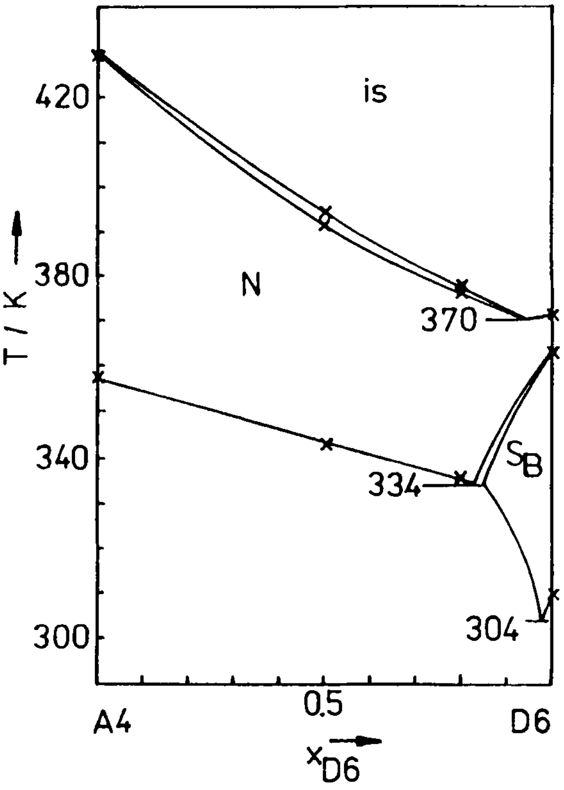


FIGURE 14 Phase diagram of **A4** and trans-4-*n*-octylcyclohexane carboxylic acid **D6**.

the shift we have the indication for an associate of a different nature which should be the heteromolecular associate between **A3** and **D1**.

Figure 15b shows that the band at 940 cm^{-1} becomes asymmetrically in the isotropic phase. Furthermore the signal at 968 cm^{-1} becomes more pronounced. Thus, the associates break apart to a higher degree than in the pure acid with increasing temperature. It seems that the heteromolecular associate **D1A3** is thermodynamically less stable than the homomolecular **D1D1**.

In general, the same effects were found using the ketone **A1** as the proton acceptor compound. The ketone itself does not show any changes with temperature in the region of interest. Figure 16 shows the temperature dependence of the mixture with $x_{D1} = 0.5$. Due to the overlapping with bands of the ketone itself we cannot give any more detailed comments about the nature of the associates.

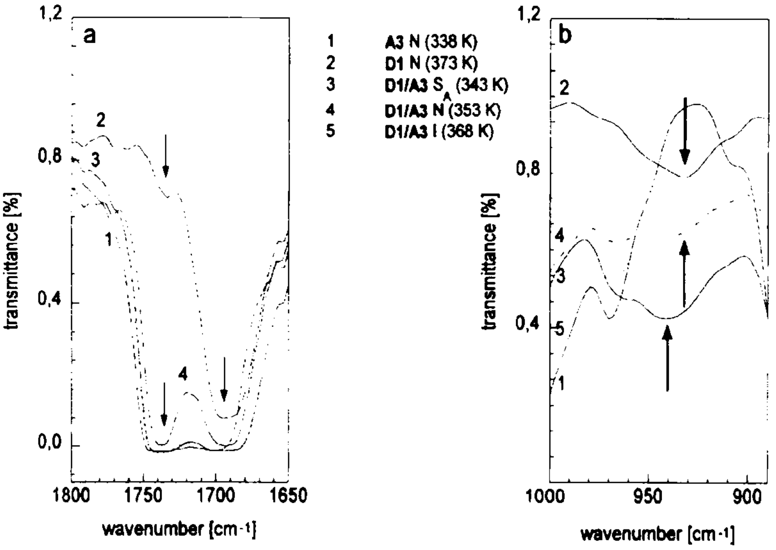


FIGURE 15 Comparative IR spectra of **D1**, **A3** and the mixture $x_{\mathrm{D1}} = 0.45$ of both at different temperatures, a) around the C=O vibration and b) the COH deformation band.

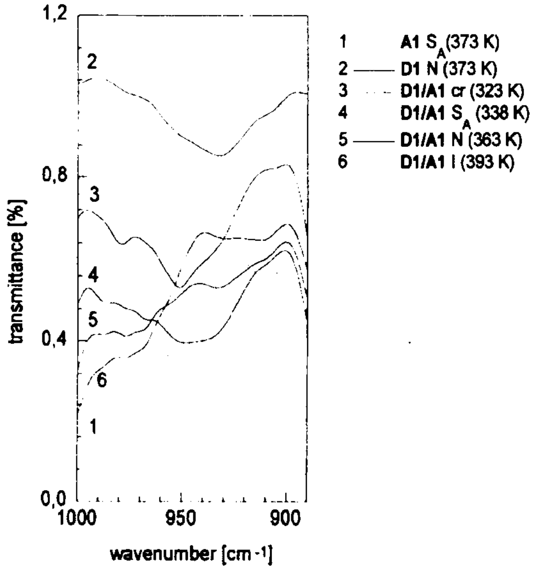


FIGURE 16 IR spectra of **A1**, **D1** and a mixture with $x_{\mathrm{D1}} = 0.5$ around the COH deformation range.

The spectroscopic results show that the associates in the 1:1 mixtures are, to a certain degree, heteromolecular. The heteromolecular associates are thermodynamically less stable, specially with increasing temperature, than the associates in the pure carboxylic acid. The coexistence of the different associates should be also the reason, that we could not detect any evidence for two eutectic points in the melting curves.

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