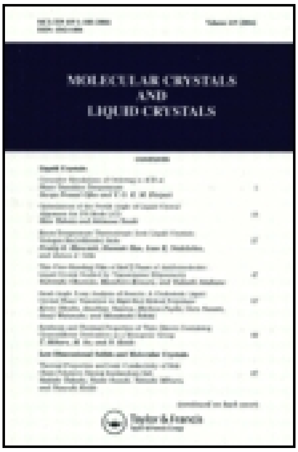

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Construction of Polycatenar Mesogens Exhibiting Columnar Phases by Hydrogen-Bonds

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CONSTRUCTION OF POLYCATENAR MESOGENS EXHIBITING COLUMNAR PHASES BY HYDROGEN-BONDS

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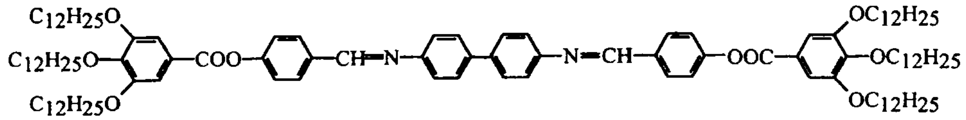
Abstract Hydrogen-bonded associates of 4,4'-bipyridine and substituted benzoic acid with a special shape exhibit columnar mesophases.

INTRODUCTION

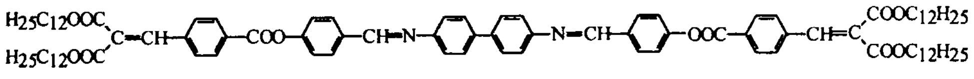
Polycatenar mesogens are derived from rod-like molecules bearing more than one carbon chain at the terminal phenyl rings[1]. These mesogens are of a great interest because of their unusual polymorphism and reentrant behavior[2,3]. Nematic, smectic, cubic as well as columnar phases can exist at single substances. Therefore, the gap existing between lamellar and columnar mesophases can be filled. Another subject of increasing interest is the formation of liquid crystals from small building units which are connected by hydrogen bonds[4,5,6]. A useful way to construct associates is the interaction of pyridines and carboxylic acids[7]. Recently, relationships between the electron-accepting or electron-donating properties of substituents attached at the benzoic acid and the tendency to form mesophases with pyridines were correlated by us[8]. Using this concept, the well-directed construction of mesogens exhibiting columnar phases by means of singular hydrogen bonds is described in the present paper.

PHASE INDUCTION

Typical examples for polycatenar compounds are phasmids (hexacatenar type) e.g. compound **1**[9] and double-swallow-tailed compounds (tetracatenar type) e.g. compound **2**[10]. The polymorphism of both is given below the formulae.



Cr 72 D_{ob} 146 I **1**



Cr 111 D_{ob} 206 I **2**

As an intellectual experiment we cut the molecules at both azomethine groups and replace them by a hydrogen bond. Therefore, we used the proton accepting 4,4'-bipyridin (A) as the central core. The side cores were realized by the corresponding benzoic acids as proton donators (D). In that way we „replaced" the azomethine group by a COOH···N interaction.

In figure 1 the phase diagram of 4,4'-bipyridin (A) and 4-(3,4,5-tri-n-dodecyloxybenzoyloxy)benzoic acid (D) is shown.

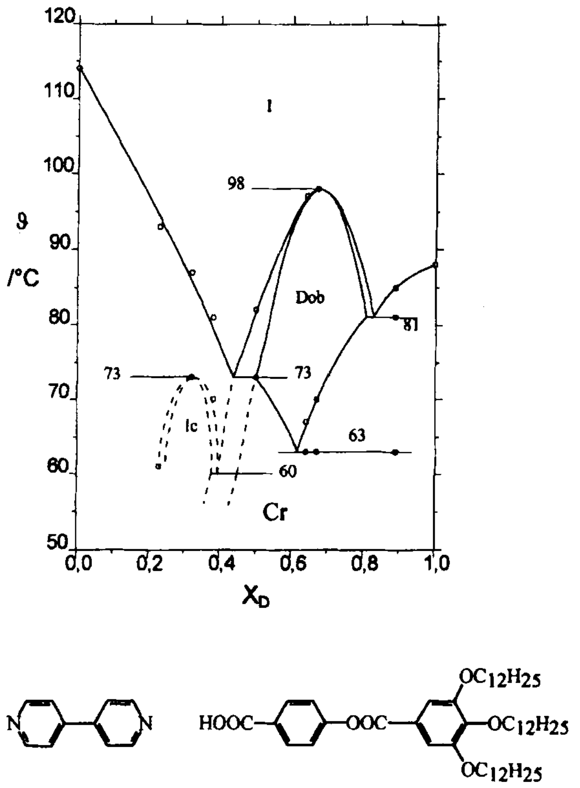


Figure 1: Phase induction at a phasmidic associate

At a concentration of 67% of acid a liquid crystalline phase with a clearing temperature of 98°C is formed. This experiment confirms the existence of a 2:1 (D:A) associate with a phasmidic molecular shape. The phase type was classified by mixing this associate D_2A with compound **1**. The complete miscibility with the D_{ob} phase of sample **1** is demonstrated in figure 2. Phase diagram 2 confirms that the thermodynamically stable induced phase is a D_{ob} one. A second liquid crystalline phase, which is metastable, was detected at 33% of acid. It is not characterized because of its strong tendency to crystallize.

Compound **2** is a typical example for the tetracatenar type. To reconstruct this from smaller building units we used the same way than in case of the hexacatenar compound. The azomethines were „replaced“ by two hydrogen bonds. The phase diagram of the respective fragments confirms the assembling of an associate and is shown in figure 3.

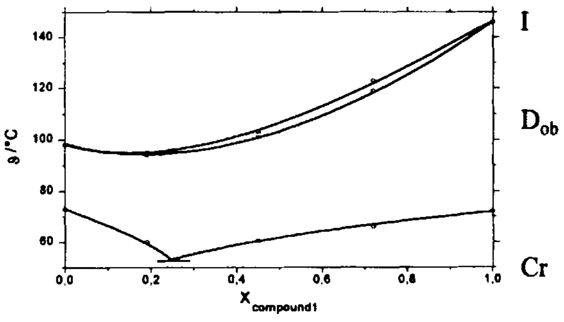


Figure 2: Phase diagram of the hydrogen bonded associate mixed with compound 1

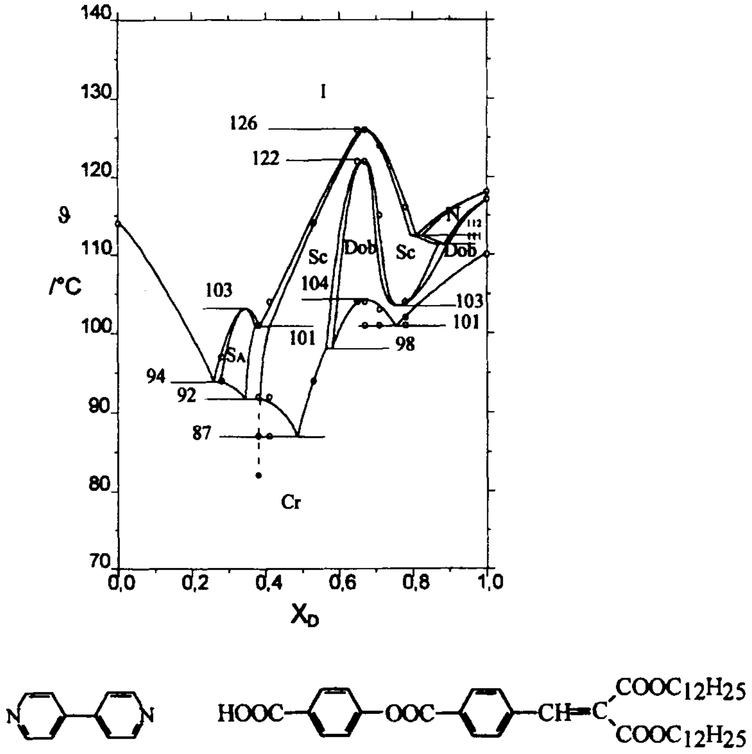


Figure 3: Phase induction at a double-swallow-tailed associate

The proton donating acid exhibits a D_{ob} phase itself which is destabilized by addition of small concentrations of 4,4'-bipyridine and becomes stabilized at the molar relation of

2:1 (D:A). The stabilization of the D_{ob} phase is connected with the induction of a S_C phase.

We want to point out, that at a concentration of 33% of acid a S_A phase is induced. It is known that the S_C phase of double-swallow-tailed compounds is able to intercalate small molecules and to form „filled" phases. In dependence of the relation between the length of the molecular core of the double-swallow-tailed compounds and the length of the guest molecules more than one of the last mentioned ones can be included[11].

CONCLUSIONS

Comparing the mesophase behavior of the associates and of the reference substances two tendencies can be discussed. The mesophase stability of the hydrogen bonded systems is lower and the tendency to organize themselves to columnar phases is decreased. This is in agreement with change of the liquid crystalline behavior of double-swallow-tailed mesogens if flexible segments like ethylene groups are inserted into the molecule[12]. Nevertheless the polymorphism of the hydrogen bonded associates is in good accordance to the reference substances. So it seems to be possible to check up the properties of mesogens before synthesizing using a „box of bricks".

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