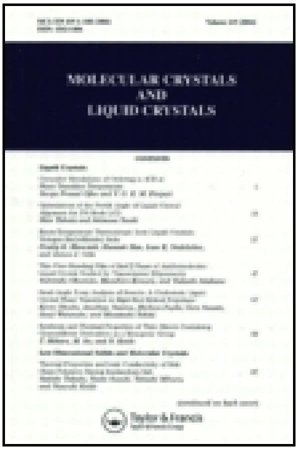

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Liquid Crystalline Properties of 2-(trans-4-n-Alkylcyclohexyl)-Propane-1,3-Diols

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LIQUID CRYSTALLINE PROPERTIES OF 2-(trans-4-n-ALKYLCYCLOHEXYL)-PROPANE-1,3-DIOLS

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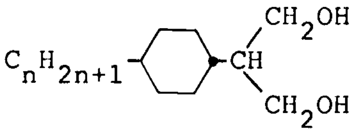
Abstract: The liquid crystalline properties of the homologous series of 2-(trans-4-n-alkylcyclohexyl)-propane-1,3-diols 1 is described. These compounds exhibit thermotropic and after addition of small amounts of water also lyotropic liquid crystalline properties. The phase behaviour is described and explained by a general model, whereby hydrogen-bonding and hydrophobic interactions are considered.

INTRODUCTION

Recently, the termotropic liquid crystalline behaviour of some 2-(trans-4-n-alkylcyclohexyl)-propan-1,3-diols has been described and the liquid crystalline phases have been investigated by X-ray analysis [1,2]. We have synthesized additional members of this homologous series and have studied their behaviour in the presence of water.



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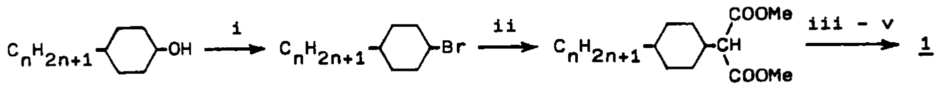
EXPERIMENTAL

The new compounds have been synthesized according to the following procedure[3].



i: PBr_3; ii: $Na^{+-}CH(COOMe)_2$, MeOH; iii: $LiAlH_4, Et_2O$; iv: H^+, H_2O; v: separation of isomers

Thereby mixtures of stereoisomers result, from which the desired trans-isomers 1 have been isolated by repeated recrystallization from n-hexane and methanol. The phase transition temperatures have been determined by polarizing microscopy. Sealed tubes have been used for the determination of the clearing temperatures of the water saturated samples.

RESULTS

The transition temperatures of the compounds investigated are given in figure 1.

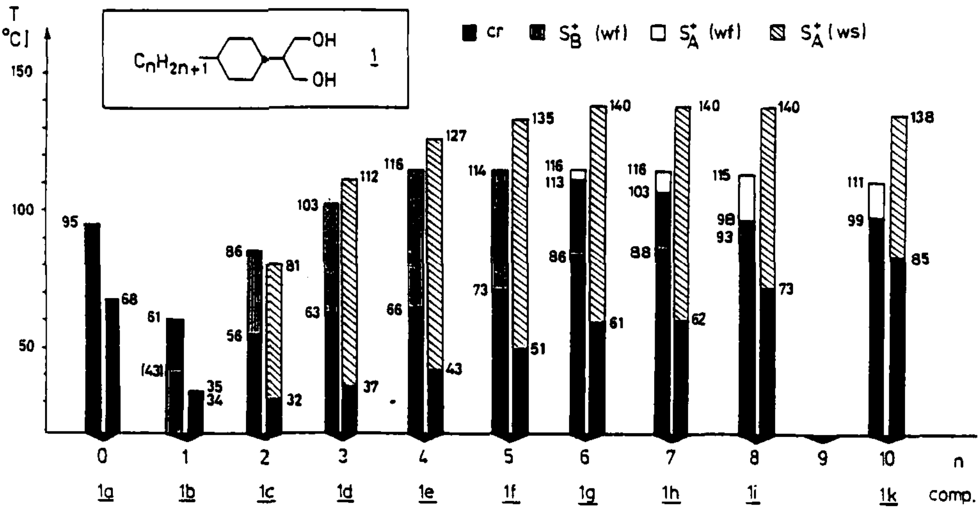


FIGURE 1: Transition temperatures of the 2-(trans-4-n-alkylcyclohexyl)-propane-1,3-diols 1 in the water-free state (wf; left columns) and in the water-saturated state (ws; right columns)

All compounds with an alkyl chain attached to the cyclohexane ring exhibit thermotropic liquid crystalline properties. The clearing temperatures strongly increase with increasing chain-length until a maximum is reached at a chain length of 6 - 8 carbon atoms. Afterwards the mesophase stability slowly decreases. It is remarkable that the short chain derivatives up to n = 5 exhibit only the S_B^+-phase, while the S_A^+-phase appears at a chain length of at least 6 carbon atoms and supresses the S_B^+-phase as the chain length grows and finally compound 1k exhibits the S_A^+-phase only.

This is contrary to the behaviour, observed for the homologous series of n-alkane-1,2-diols[4], where the S_A^+-

phase disappears with increasing chain length. Therefor we must conclude that both types of $S_B{}^+$-phases differ substantially in their structures: The hexagonal order in the case of compounds 1 is mainly determined by the cyclohexane ring, whereas in the case of the n-alkane-1,2-diols the hexagonal order must be realized by ordering the alkyl chains.

The addition of small amounts of water causes significant changes in the mesophase behaviour. These materials take up approximately 1,5 mol water/mol 1 to give a melting point depression of 14-26K and a clearing temperature enhancement, if the terminal chain length exceeds n=2. The mesophases of the methyl and ethyl substituted derivatives 1b and 1c are depressed by the addition of water, while in all other cases the mesophases are stabilized. Thereby the mesophase stabilization increases with growing alkyl chain length (Figure 2), and the clearing temperatures of the water-saturated samples reach a maximum at n = 6-8.

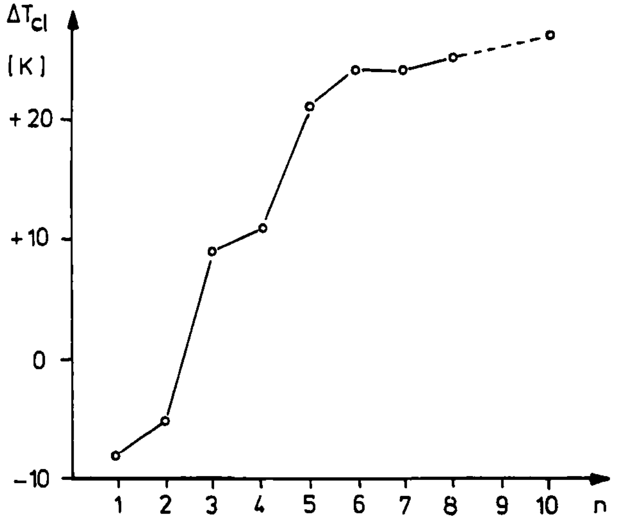


FIGURE 2 Dependence of the maximal possible mesophase (de)stabilization of the compounds 1 by addition of water (T_{cl}, max ($1+H_2O$) $-T_{cl}(1)$) from the chain length (n).

All water-saturated samples exhibit mesophases which could be classified by polarizing microscopy as $S_A{}^+$-phases. Fan-like textures with homeotropic regions and oily streaks can be observed.

To study the influence of water on the phase behaviour in more detail the phase diagram of compound 1i (Figure 3) was constructed from dsc data as described in the previous paper[5].

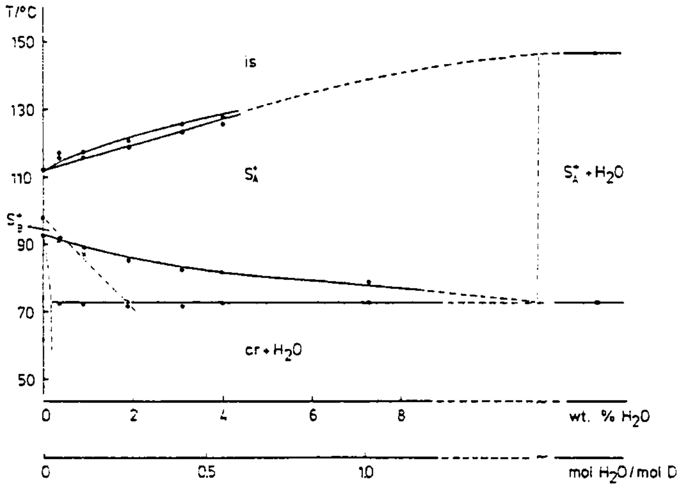
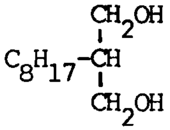
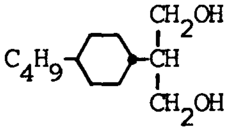


FIGURE 3 Phase diagram of the system 2-(trans-4n-octylcyclohexyl)-propane-1,3-diol (1i)/water.

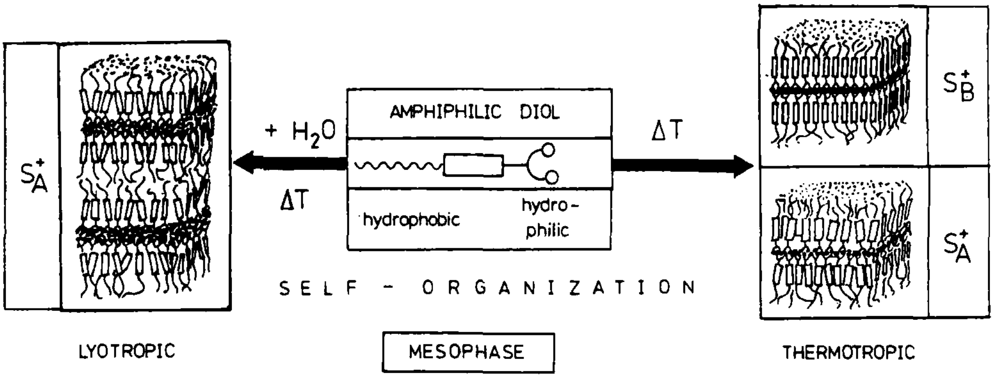
The water-free sample exhibits the S_B^+ and S_A^+ phase between the crystalline and the isotropic state. S_B^+ - S_A^+ shifts to lower temperatures with increasing water content of the sample. Between 0.5 and 2 wt.% of water a monotropic S_B^+ phase can be found on cooling. Above 2 wt.% of water only the S_A^+ phase exists between the crystalline and the isotropic state. The clearing temperature shifts to higher temperatures with increasing water content. The aluminium dsc pans could be used only below 130°C. Therefore the clearing point in the water-saturated region was observed by microscopy. The water-saturated sample was sealed in a glass tube. The crystallization of the samples is connected with an almost complete dehydration of the diol head group. This dehydration is the reason for the eutectic behaviour. The comparison of the mesomorphic properties of these compounds 1 with those of the 2-n-alkyl-propane-1,3-diols[6] indicates the strong mesophase stabilization effect of the cyclohexane moiety: While compound 2 exhibits no mesophase in the water-free state, the cyclohexane derivative 1e has a broad thermotropic mesomorphic range.

	 $\begin{array}{c} CH_2OH \\ \mid \\ C_8H_{17}-CH \\ \mid \\ CH_2OH \end{array}$	
water-free state:	m.p.:47°C	cr 66 S_B^+ 116 is
water-saturated state:	cr 30 L_α 50 is	cr 43 S_A^+ 127 is

The stability of the lyotropic mesophase is largely enhanced in this way too.

DISCUSSION

These results are in line with our model: Thereby the hydroxy groups of the amphiphilic diols are organized in large hydrogen bonded networks which are arranged in double layers forming parallel equidistant sheets separated by the hydrophobic chains:



The introduction of one cyclohexane-ring into the hydrophobic chain causes a significant mesophase stabilization due to the restriction of their flexibility and by increasing the Van der Waals interactions between them.

The different influence of water upon the mesophase stability could be explained in the following way: The hydrogen bonding is a directed interaction. This means that there are some favoured conformations for an optimal interaction between two hydroxy groups. Thus the participating hydroxy group and one lone pair at the oxygen atom should be ordered in a strictly linear manner to get the best interaction. This favoured conformation is not realized for all hydrogen bonds

in the associates at the same time. If water molecules are added, these will be built into the hydrogen bond framework and thus stabilize the aggregates by increasing the number of optimal hydrogen bonds.
But with the increasing number of water molecules associated with the diol structural unit, the size of the diol group also increases. In this way the hydrophobic chains are separated from each other and the resulting free space must be filled by increasing molecular motion what means that the hexagonal arrangement in the $S_B{}^+$-phase is disfavoured with increasing water content of the sample.
If the hydrophobic part of the amphiphilic diols is very short and rather stiff the increased intermolecular distance between the hydrophobic chains cannot be compensated by additional conformational motion and in these few cases (compounds 1b and 1c) the addition of water decreases the mesophase stability because the stabilization of the associates by increasing hydrogen bonding is overcompensated by the weakening of the hydrophobic interactions.

REFERENCES

1. S. Diele, E. Geissler, H.-M. Vorbrodt and H. Zaschke, Mol. Cryst. Liqu. Cryst. Lett. 102, 181 (1984)
2. S. Diele, A. Mädicke, E. Geissler, K. Meinel, D. Demus and H. Sackmann, Mol. Cryst. Liqu. Cryst. 166, 131 (1989)
3. D. Demus, H. Zaschke, S. Deresch and H.-M. Vorbrodt, DD 207 308
4. C. Tschierske, G. Brezesinski, F. Kuschel and H. Zaschke, Mol. Cryst. Liqu. Cryst. 6, 139 (1989)
5. G. Brezesinski, A. Mädicke, C. Tschierske, H. Zaschke and F. Kuschel, Mol. Cryst. Liqu. Cryst. Lett. 5, 155 (1988)
6. N. Pietschmann, G. Brezesinski, C. Tschierske, H. Zaschke and F. Kuschel, Mol. Cryst. Liqu. Cryst. Lett. (submitted for publication)