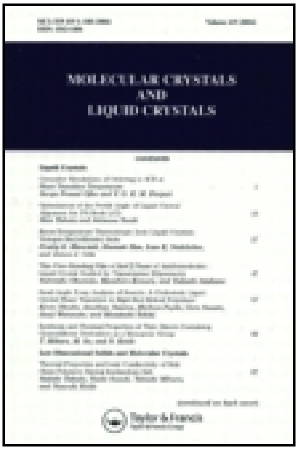

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Monolayer Properties and Lyotropic Phase Behaviour of Liquid-Crystalline 1,3-Diols

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To cite this article: W. Rettig , G. Brezesinski , A. Mädicke , C. Tschierske , H. Zaschke & F. Kuschel (1990): Monolayer Properties and Lyotropic Phase Behaviour of Liquid-Crystalline 1,3-Diols, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 115-120

To link to this article: http://dx.doi.org/10.1080/00268949008031812

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 115–120
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Printed in the United States of America

MONOLAYER PROPERTIES AND LYOTROPIC PHASE BEHAVIOUR OF LIQUID-CRYSTALLINE 1,3-DIOLS

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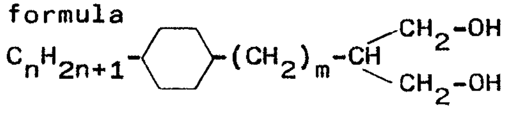
Abstract The influence of a cyclohexane ring at various locations along the alkyl chain on the monolayer and bulk phase properties of isomeric propane-1,3-diols is discussed. The addition of water stabilizes the liquid-crystalline behaviour remarkably. The monomolecular films are of the condensed type.

INTRODUCTION

The investigation of simple 2-n-alkyl-propane-1,3-diols revealed that these compounds exhibit a liquid-crystalline behaviour only in the presence of water [1]. The capability of self-organization leads to the formation of monolayers at the air-water interface with a pronounced film polymorphism [2]. The incorporation of the cyclohexane ring in the alkyl chain effects the occurrence of liquid-crystalline phases already in the water-free state [3]. The present study deals with the effect of an incorporated cyclohexane ring at various locations along the alkyl chain on the monolayer and bulk phase properties of isomeric propane-1,3-diols with the general formula



$$C_nH_{2n+1}\text{-}C_6H_{10}\text{-}(CH_2)_m\text{-}CH(CH_2\text{-}OH)_2$$

, where n+m = 8.

EXPERIMENTAL

The calorimetric studies were performed using a Perkin-Elmer DSC-2. The texture observations were carried out on a polarizing microscope equipped with a hot stage. The compression curves (F/A-isotherms) were taken on a home made Langmuir balance (Wilhelmy-type) equipped with continuous measuring system [4]. The films were spread from a hexene solution (~1 mg/ml) and were compressed continuously ($0.01\ nm^2 \cdot molecule^{-1} \cdot min^{-1}$). The measurements were performed at 22 °C. The temperature was kept constant within 0.2 °C.

RESULTS and DISCUSSION

The bulk properties were investigated both in the water-free state and in the presence of excess water (50 wt.-%). On the base of texture observations the mesophases were preliminary designated as S_A^+ and S_B^+. The cross indicates that the smectic phases do not show a complete miscibility with conventional liquid crystals.

The methylene units between the propane-1,3-diol and the cyclohexane ring may be considered as a spacer which decouples these two parts of the molecule. At first, the decoupling leads to a stabilization of the mesophase behaviour in both the water-free and the water-saturated state. The compounds with an odd-numbered spacer exhibit the broader mesophase range. The further shifting of the cyclohexane ring towards the end of the alkyl chain destabilizes the mesophase behaviour.

The addition of water leads to a remarkable stabilization of the liquid-crystalline behaviour. The melting points are decreased and the clearing points are increased in the presence of excess water. From Figure 1(b) it becomes evident that the higher ordered

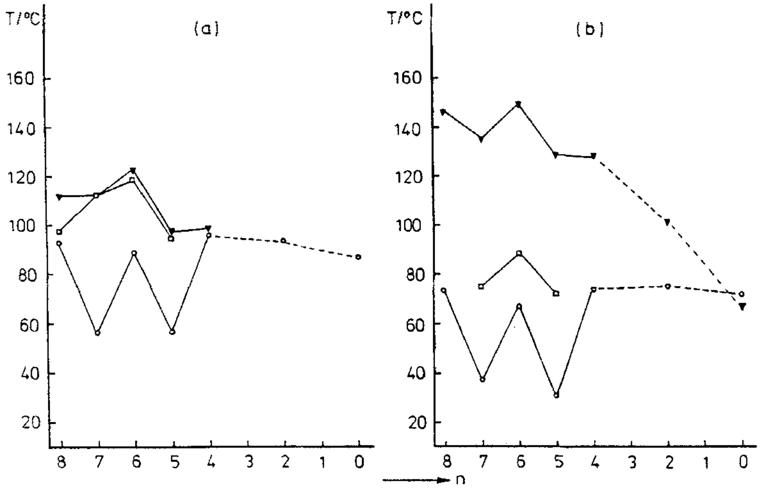


FIGURE 1 Transition temperatures as a function of the location of the cyclohexane ring. (a) water-free state, (b) water-saturated state. ○ = melting point; ▼ = S_A^+ - isotropic; □ = S_B^+ - S_A^+ or S_B^+ - isotropic.

S_B^+-phase is destabilized in the presence of water, whereas the S_A^+-phase is stabilized or induced by addition of water. On cooling the compound with n = 0 from the isotropic state a monotropic S_A^+-phase appears.

The monolayers characterized by the compression curves at T = 22 °C, which are represented in Figure 2, indicate that the diols investigated form only condensed films in the temperature range up to 50 °C. The diols with n = 4-6 show a transition within the condensed films. It seems that the compound with n = 4 exhibits a first-order transition. On the other side, the n-alkyl-propane-1,3-diols [2], which show a similar film polymorphism as the n-alcohols [5], form mainly liquid-expanded films in the temperature range investigated. This observation indicates that the cyclohexane ring

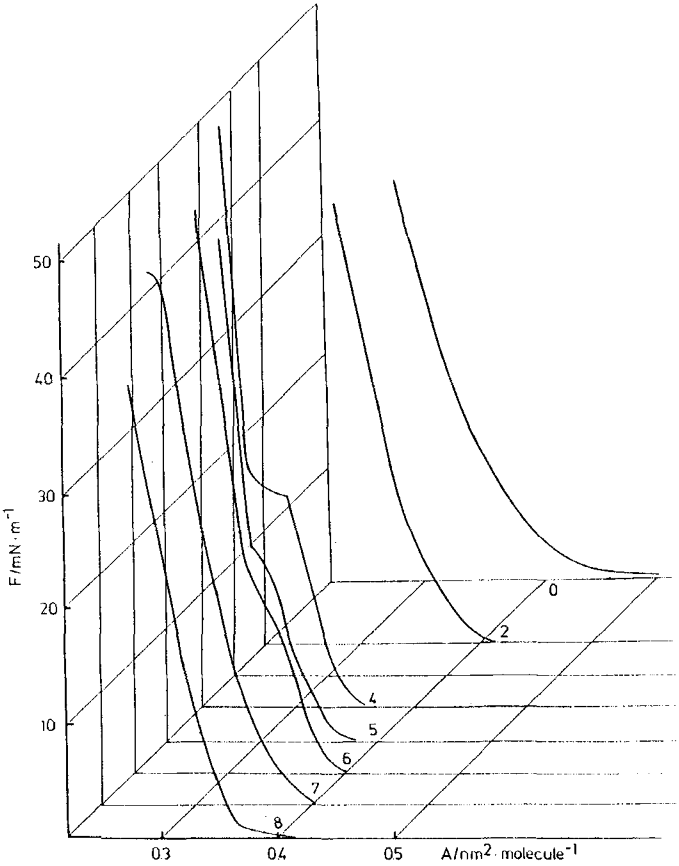


FIGURE 2 F/A-isotherms as a function of the location of the cyclohexane ring.

has a strong condensing effect. The assumption is supported by the experimental fact that n-octyl-cyclohexyl-methanol (M8) can only form condensed films, while n-dodecanol, which has nearly the same chain length as M8, forms liquid-expanded films at T = 22 °C.

To discuss the monolayer properties in more details the parameters (see Figure 3) proved useful in analysing the isotherms are compared with those of similar compounds. The following results could be obtained:

The film behaviour depends sensitively on the location of the cyclohexane ring. If it is located in the middle part of the chain (n = 4-6) a transition into a more densely packed condensed film occurs and the highest film pressures are observed.

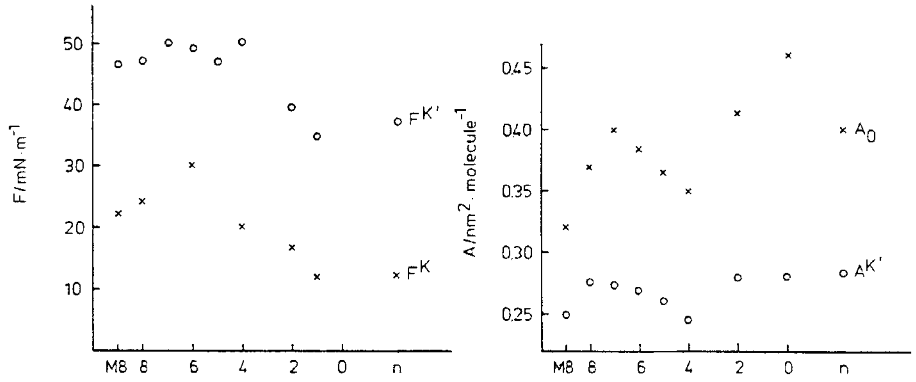


FIGURE 3 Characteristic film pressures and molecular areas of isomeric propane-1,3-diols. For M8 see text.
A_o = lift-off area [5]; $A^{K'}$, $F^{K'}$ = molecular area and film pressure at densed packing, values used from the compression curve where the film ruptures; F^K = equilibrium collapse pressure [4].

M8 and the homologous n-alkyl-propane-1,3-diols [2] occupy the same molecular area at densed packing (0.24 - 0.25 nm^2) in the condensed films. In the case of M8 the $A^{K'}$-value is determined by the cyclohexane ring, whereas the $A^{K'}$-value of the n-alkyl-propane-1,3-diols is determined by the head group. It is interesting that the direct linkage of the both moities leads to an increase of the characteristic area values (compounds with n = 8,7). This may be explained by an extreme hindrance to free rotation of these groups.

If the spacer increases, the molecular areas $A^{K'}$ and also A_0 decrease and reach nearly the molecular area of the both moities. However, if the spacer becomes larger than m = 4, the areas increase. This is accompanied by a decrease of the film pressure indicating that the condensed films were destabilized.

From the strong influence of the location of the cyclohexane ring on both the bulk phase and the monolayer properties the question arises of whether the arrangement of the molecules in the layers also depends on the location of the ring. This problem is presently under investigation.

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