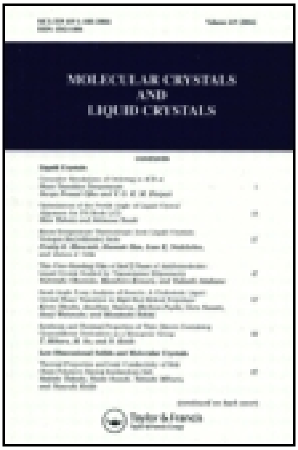

Molecular Crystals and Liquid Crystals

Shape-Persistent Macrocycles with Adaptable Units: New Insights from the Solid State

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SHAPE-PERSISTENT MACROCYCLES WITH ADAPTABLE UNITS: NEW INSIGHTS FROM THE SOLID STATE

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Shape-persistent macrocycles are described in which the orientation of the side groups is not determined by the synthesis, but can be influenced by an external parameter such as solvent polarity (adaptable side groups). In the case of amphiphilc macrocycles, a polar solvent induces a conformation in which the polar side groups point to the exterior of the molecule. Whereas in a less polar solvent in the presence of appropriate guest molecules an inverse conformation is observed where the polar side groups point to the interior of the molecule. The ability of the adaptable side groups to rotate freely lead also to the investigation of the first discotic liquid crystals with an inverse topology, namely composed of an rigid corona and a flexible core.

Keywords: adaptable structures; discotic liquid crystals; host-guest chemistry; macrocycles

INTRODUCTION

Shape-persistent macrocycles are composed of a rigid backbone having a lumen in the range of one up to several nanometers. The diameter of the ring can be estimated roughly by the contour length of the backbone divided by π. Due to their rigidity, most shape-persistent macrocycles are only sparingly soluble in common solvents and therefore only a limited number of these structures are described which contain no solubilizing side groups. The properties and possible applications of the macrocycles

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strongly depend not only on the nature of these side groups, but also on their orientation relative to the molecular backbone. So far, in nearly all synthetic macrocyclic structures this orientation is fixed and determined by the synthetic precursors of the compounds [1]. In contrast, enzymes, rigid on first glance, often exhibit an considerable flexibility in order to function properly [2].

RESULTS AND DISCUSSION

We recently described functionalized shape-persistent macrocycles in which the orientation of the functional groups relative to the molecular backbone is not determined by the synthesis, but can be influenced by an external parameter [3]. The macrocycles are based on the phenyl-ethynyl backbone and depending on the position where the side groups are attached to the ring they point either to the inside (I, I′), to the outside (E, E′), or they are in an adaptable arrangement (A, A′) (Fig. 1).

The synthesis of the molecules is based on the oxidative acetylene coupling under pseudo-high dilution conditions that can be performed either in a statistical way or using the template supported route. These methods allow the preparation of a variety of different macrocycles in good to high yields [4].

Recrystallization of compound **1** (Fig. 2) from the polar solvent pyridine leads to crystals suitable for single-crystal x-ray analysis. Per macrocycle, eight molecules of pyridine act as a solvate in the crystal. Four of them are bound via hydrogen bonds to the polar pheno-OH groups of the ring, the

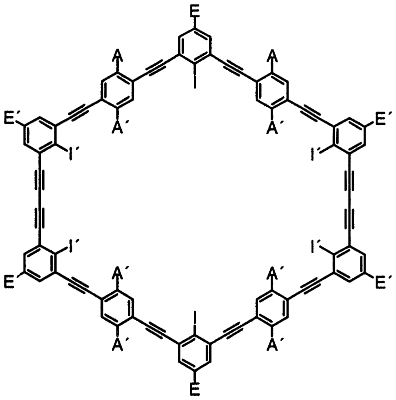

FIGURE 1 Schematic representation of the macrocycles.

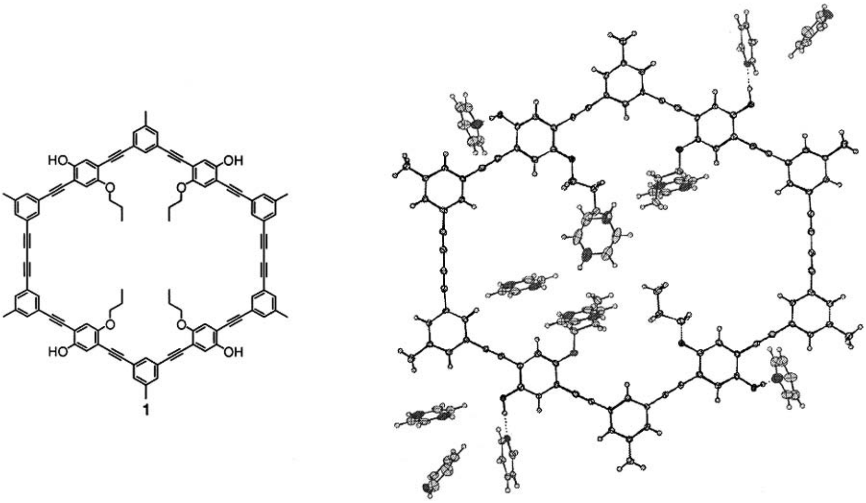

FIGURE 2 Structure of **1**.

other four have no specific interaction with the macrocycle. Of special interest is the fact that the macrocycle adopts a conformation in which the adaptable polar phenol-OH groups point to the outside and the ring has a non-polar interior in crystals grown from pyridine solvent (Fig. 2) [3].

The ability of this class of macrocycles to adopt an opposite conformation was investigated by the interaction with appropriate guest molecules. The latter contain hydrogen-bonding acceptor groups located such that they can interact with the phenol-OH groups of the ring if these point to the inside. In order to limit hydrogen bonding interactions with the solvent, the binding constants were determined in tetrachloroethane. The stronger binding constant for the smaller guest molecule (GUEST 1), together with the independent proof that host and guest form a 1:1 complex, is a strong indication that the guest molecule forms a host-guest complex with the guest molecule located inside the host molecule (Fig. 3). This is only possible if the polar phenol OH-groups of the ring point inwards. Since this conformation is opposite to the one found for **1** in the solid state, it is proven that the conformation of this adaptable amphiphiles can be influenced by an external parameter [3].

The ability of the central aromatic structures of the sides of **1** and related structures to rotate freely has also a strong influence on the properties of non-polar shape-persistent macrocyles.

Mitsunobu reaction of **1** with octadecanol leads to the corresponding tetrakis(octadecyl) ether **2**. **2** and the independently synthesized **3** are

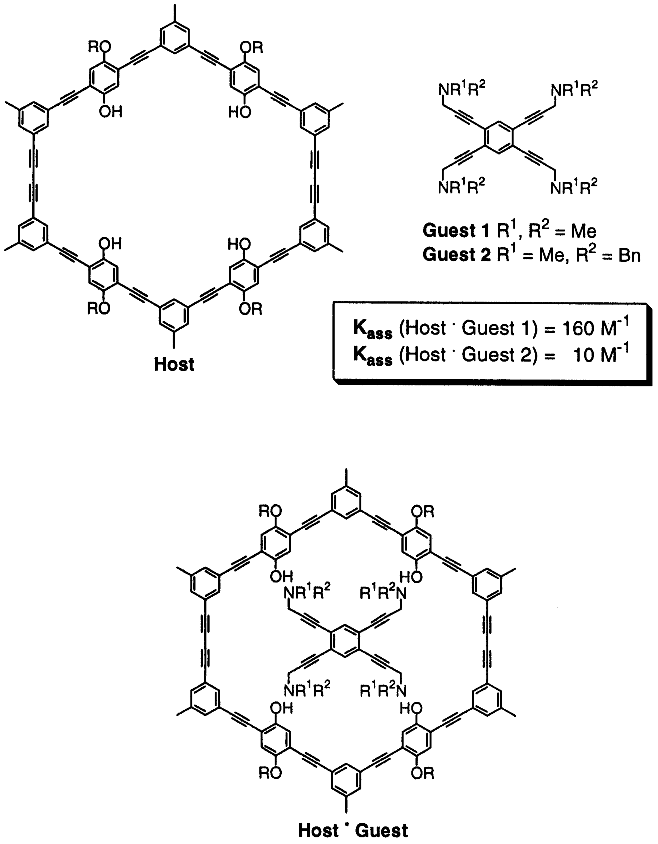

FIGURE 3 Host-guest interactions and structure of the host-guest complex.

isomers at first glance (Fig. 4) [5]. Both compounds fulfill, at least on paper, the design principle of discotic liquid crystals: they are composed of a rigid core surrounded by a flexible alkyl periphery [6]. Contrary to our expectations, **3** melts isotropically at about 220°C. However, **2** melts at 185°C and forms a nematic mesophase that becomes isotropic at 207°C. A possible explanation for the higher melting point of **3** is the following. Since both compounds are solvent free in the solid state, the interior of the rings has to be filled with alkyl chains. In the case of **3** a backfolding of the alkyl chains is rather improbable and therefore the interior of one ring is filled by the alkyl chains of neighboring rings leading to an interlocking of the molecules. However, **2** has another possibility to fill the empty interior. Single-crystal x-ray analysis shows it adopts in the solid state a conformation in which the long alkyl chains do not point to the outside but fill the *own*

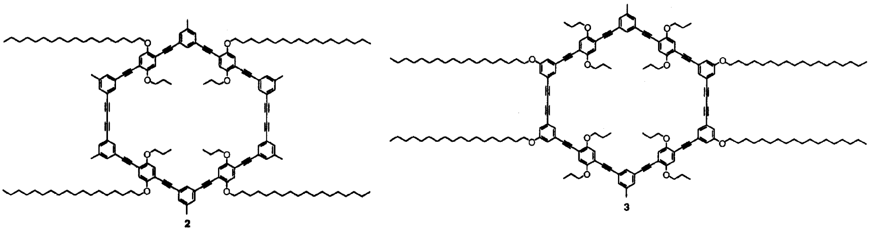

FIGURE 4 Macrocycles **2** and **3**.

interior (Fig. 5). Therefore, the cavity of **2** does not act as physical crosslinker. Again, the origin for this behavior is the ability of the central aromatic units of the sides of this macrocycles to rotate freely, allowing the substituents at these positions to point inwards or outwards, depending on external conditions.

It must be pointed out that even more important is the fact that the ring has a conformation which is opposite to all discotic liquid crystals described before: it is composed of a rigid periphery and a flexible inside.

However, the ability of the central aromatic rings of **2**, and therefore of the octadecyl side chains, to point inwards or outwards gives rise to a new question. It is not clear if the macrocycles adopts the same conformation in the nematic liquid crystalline phase (at 470 K) which is found in the solid state (recorded at 165 K). An answer to the question if liquid crystallinity is compatible with a structure composed of a rigid periphery and a flexible core will be given by the synthesis of macrocycles in which the alkyl groups are then attached such that they point to the inside and can not rotate outwards (at the positions I, I′ in Fig. 1). The synthesis and investigation of these structures is in progress.

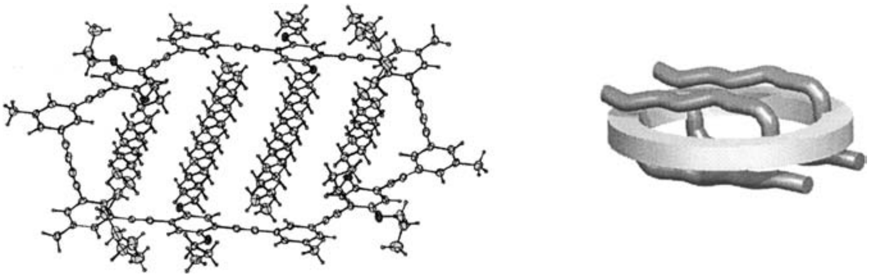

FIGURE 5 X-ray analysis of **2** and the schematic structure description.

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