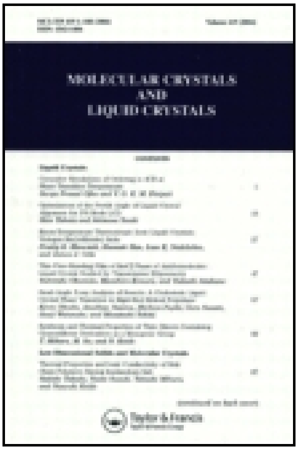

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Controlled Orientation of Metalloporphyrins and Regioselective Epoxidations in Thermotropic Liquid Crystals

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CONTROLLED ORIENTATION OF METALLOPORPHYRINS AND REGIOSELECTIVE EPOXIDATIONS IN THERMOTROPIC LIQUID CRYSTALS

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Abstract The orientation of a porphyrin molecule in a thermotropic nematic liquid crystal can be controlled by molecular design. Thus, the porphyrin plane of tetraphenylporphyrin (TPP) is aligned parallel to the director of a liquid crystal whereas a porphyrin with orthogonal substitution of mesogenic 4-n-butoxybiphenyl appendages (MesogenP) is oriented in a perpendicular conformation. The alignment was determined by time resolved EPR spectroscopy of the triplet state of the free base porphyrin. Manganese TPP and MesogenP porphyrins then were used as catalysts for the epoxidation of alkenes using iodosobenze as oxidant. Reaction yields and regioselectivity for enlongated substrates such as *cis*-stilbene and 4-vinylbiphenyl were dependent on the alignment of the alkene and its carbon-carbon double bond relative to the director and metalloporphyrin catalyst.

INTRODUCTION

Catalysis deals both with rate enhancement and regio- and stereoselectivity of reactions. In recent years there has been a great interest in the chemistry of metalloporphyrins due to their unique ability to catalyse the oxidation of hydrocarbons, both alkenes and alkanes, at ambient temperatures with numerous oxidants[1]. Stereoselectivity, for example *cis*-epoxides from *cis*-alkenes, has been obtained by synthesis of porphyrins with a hindered active site[2]. Enanatioselectivity has also been achieved with relativally high enantiomeric excesses by attaching chiral appendages to the porphyrin moiety[3]. A more elusive task is to induce regioselective reactions such as alkene epoxidation in compounds having two or more similar carbon-carbon double bonds. In our first study in this field a steroidal porphyrin was synthesized which enabled its specific orientation in liposomal bilayers and allowed regioselective oxidation of amphiphilic substrates[4]. We are now extending our research into the oxidation by metalloporphyrins of nonpolar hydrocarbons in thermotropic liquid crystals. This study of reactions in organized media such as thermotropic liquid crystals are of great current research interest[5] and will enable us to understand the importance of organization of subtrates and catalysts in chemical reactions. In this context, an understanding of the chemistry of porphyrins and metalloporphyrins is of special relevance due to the part these compounds play in additional processes such as photosynthesis[6], and dioxygen and electron transport[7].

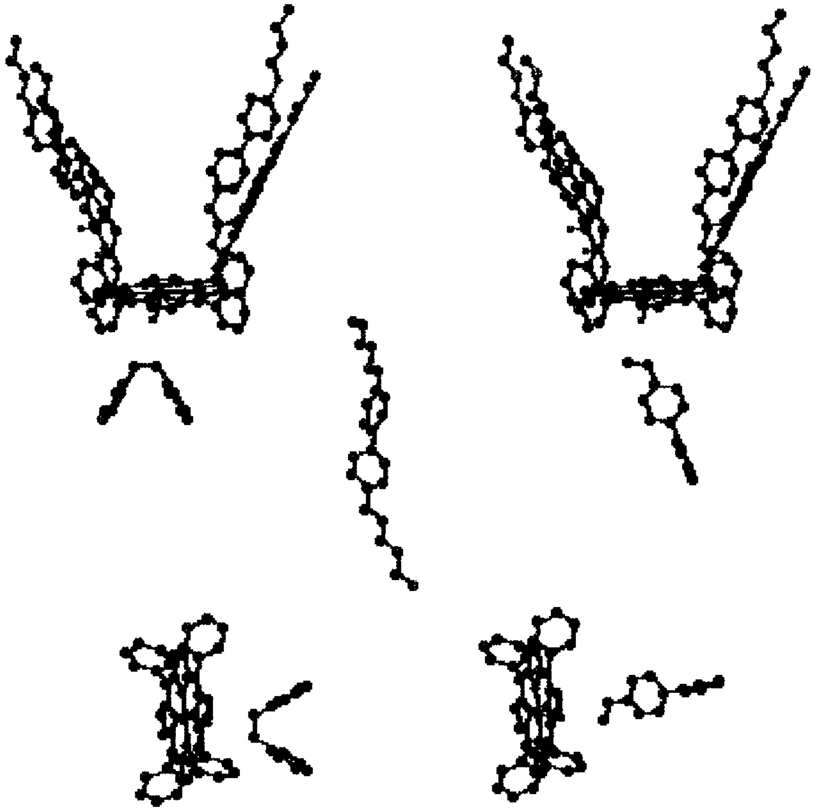

FIGURE 1 Illustration of substrate interaction with oriented metalloporphyrins in a nematic liquid crystal phase.

RESULTS AND DISCUSSION

In the past, we have been able to acheive control of porphyrin orientation in thermotropic[8] liquid crystals host phases by attaching molecularily compatible (to the host) appendages to the porphyrin ring. In a nematic thermotropic liquid crystal host phase (4-cyano-4'-hexylbiphenyl (BDH K18) with K → N 14.5 °C and N → I 29 °C) a tetraphenylporphyrin (TPP) is aligned so that the porphyrin ring is parallel 0 ± 10° to the direction of the mesogenic host phase whereas for a porphyrin with mesogenic "arms" attached orthogonally to the porphyrin ring, *ie*, *meso*-tetra{α,α,α,α-*o*-[4-(4-*n*-butoxyphenyl)phenyl-acetamido]} porphyrin (MesogenP) the porphyrin ring is oriented perpendicular 85 ± 10° to the nematic host phase[8], Figure 1. These alignments were proven by evaluation of the excited triplet state ESR spectrum of the free base and zinc porphyrins.

Manganese(III) acetate porphyrins were prepared by metalation with a hundred fold excess of manganese(II) acetate in DMF reflux under air for four hours. Thus, 0.1 mmol free base porphyrin and 10 mmol $Mn(OAc)_2 \cdot 4H_2O$ were dissolved in 3 ml DMF and boiled at reflux for four hours. After cooling the porphyrins were extracted with dichloromethane and the DMF was removed by washing with water. After evaporation of the solvent the mangenese porphyrins were purified on a alumina column and were shown to be authentic Mn(III) porphyrins by their visible spectrum (λ_{max} 372, 400, 476, 576, 618 nm). Epoxidation reactions were run by mixing 0.15 mmol metalloporphyrin, 25 mmol substrate, 25 mmol iodosobenzene at 20±0.5 °C in both in a liquid crystalline 4-cyano-4'-hexylbiphenyl solvent and an isotropic dichloromethane solvent for four hours. The reactions were followed by GLC using a nonpolar methyl silicone capillary column.

The results of the competitive epoxidation of two somewhat enlongated or rod like substrates having sustrates having similar vinylic bonds, *cis*-stilbene and 4-vinylbiphenyl, reveal the essential features of the substrate, host, and porphyrin spacial interactions Figure 2. First we examined the reactivity in the isotropic solvent, dichloromethane. One can observe similar reactivity for 4-vinylbiphenyl with both MnTPP and MnMesogenP, however, with *cis*-stilbene the reactivity with the MnMesogenP catalyst is half of that found in MnTPP. We attribute this phenomenom to the steric hindrance on one side of the porphyrin plane in the MesogenP. The resulting "pocket" which is formed prevents the lateral approach of *cis*-stilbene. Since the active oxo species may be on both sides of the porphyrin ring the *cis*-stilbene epoxidation is inihibition using MnMesogenP. The *cis*-stilbeneoxide:*trans*-stilbeneoxide ratios of 3-4:1 are indicative of a catalytic system with both Mn(IV)=O and Mn(V)=O as active oxygen donors[9]. The inversion from *cis*-stilbene to *trans*-

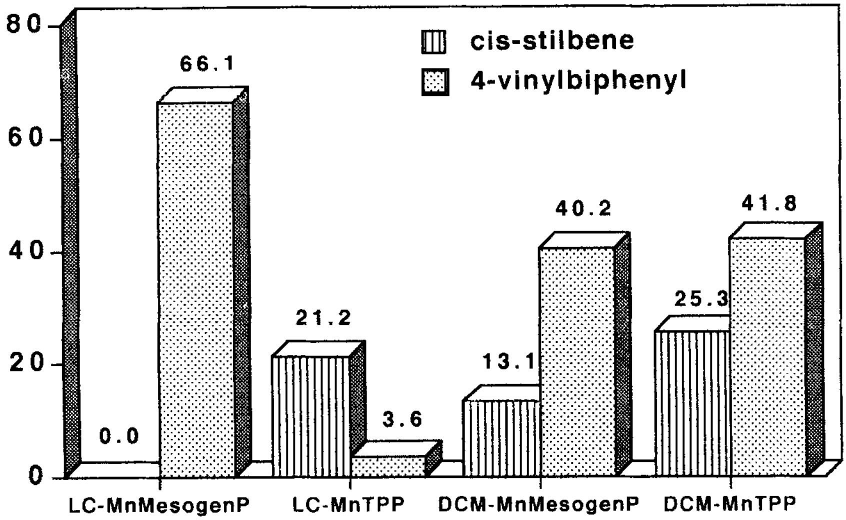

FIGURE 2 Competitive epoxidation of cis-stilbene and 4-vinylbiphenyl.

stilbene oxide also indicates a *trans* conformation of the substrate in the transition state. For reactions performed in the liquid crystal solvent, one may observe that for *cis*-stilbene where the preferred alignment of the substrate is perpendicular to that of the porphyrin ring (MnMesogenP) there is **no** reaction. The idealized relative catalyst-substrate orientations as shown in figure 1 are based on the assumption that epoxidation takes place upon interaction of a electrophilic metal-oxo species[10] and the nucleophilic π orbital (HOMO) of the alkene. When the orientation of *cis*-stilbene is parallel to that of the porphyrin as in MnTPP as catalyst there is epoxidation similar to that found in the isotropic solvent. With 4-vinylbiphenyl as substrate the prefered ideal alignment of the substrate relative to the MnTPP catalyst forces the biphenyl moiety to 60° relative to the nematic host, leading to a low yield. However, in the case of MnMesogenP as catalyst the ideal orientation of the biphenyl group is almost parallel relative to the liquid crystal host and yields are high. It is important to note that although the analysis of the results has been carried out using a idealized representation of the orientation of the catalyst and substrate, a real picture must take into account orientational fluctuations relative to the director (even if these fluctuations average out) and perturbations in the liquid crystal phase especially with MesogenP where the porphyrin ring is perpendicular to the director. Despite these limitations, however, we feel that the evidence indicates strong orientational effects.

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