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Helical twisting power of chiral titanium complexes in nematic compounds

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We report the use of chiral bis-chelated imine-alkoxytitanium complexes as dopants for the conversion of a nematic into a cholesteric phase. High helical twisting power (HTP) is obtained in the liquid crystalline mixture ZLI-1695 (Merck, Darmstadt). Enlargement of the HTP is achieved by novel analogues of the titanium complexes, whose synthesis is described.

1. Introduction

Chiral liquid crystal compounds are important in various technical applications [1]. A particularly efficient method of obtaining this type of material is the addition of an enantiomerically pure compound, a so called dopant, to a nematic phase, so that the latter is converted into a chiral nematic phase [2, 3]. As shown by Stegemeyer and Mainusch, enantiomerically pure coumpounds that do not form a mesophase are nevertheless able to function as dopants that induce helicity in a nematic phase [4]. A measure of the efficiency of a chiral dopant is the 'helical twisting power' (HTP), which is defined according to equation (1) for small concentrations of a dopant.

$$HTP = \lim_{x \to o} \frac{1}{px} \tag{1}$$

Here, p is the pitch of the induced helix and x is the molar fraction of the dopant [2]. For most applications [1] the pitch p of the helix should be in the range of the wavelength of visible light. Aside from natural products and simple derivatives thereof [4], a variety of synthetic compounds has been developed that serve as chiral dopants [5]. We have recently shown that bis-chelated titanium complexes featuring an arylphenoxy moiety exhibit very high HTP values [6] obtained in MBBA, an achiral mesophase that is, however, mainly of academic interest. In this article, we describe the determination of the HTP of chiral titanium complexes in the commercially available nematic mixture ZLI-1695 (Merck, Darmstadt) that consist of four alkyl-substituted bicyclohexylcarbonitriles (scheme 1). In addition, the synthesis of new titanium complexes with enlarged HTP values is described.

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2. Experimental

2.1. *Synthesis*

2.1.1. Aldehydes 5a and 5b (see scheme 3). A 25 ml two-neck round bottom flask was equipped with a magnetic stirrer and a reflux condenser, which was connected to the combined nitrogen/vacuum line. The flask was charged with the corresponding boronic acid **3a** or **3b** (9.4 mmol), 5-bromo-2-hydroxybenzaldehyde (1.714 g, 8.526 mmol), [Pd(dppf)Cl_2] (0.05 eq., 0.348 g, 0.426 mmol) and dry sodium carbonate (1.356 g, 12.79 mmol), and closed with a septum. The air in the flask was replaced by nitrogen and 10 ml of a degased mixture of 1,2-dimethoxyethane and water (3/1) was added via syringe. The septum was replaced by a stopper, and the mixture heated at 100°C for 5 h. After cooling to room temperature, the mixture was filtered and the filtrate poured into 50 ml of deionized water. The mixture was extracted with three 50 ml portions of dichloromethane, and the combined organic layers were dried with sodium sulfate and concentrated in a rotary evaporator. The residue was purified by column chromatography to give solid products.

5a: yield 48%, R_f=0.3 (*n*-hexane/chloroform 1/2), ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.11–7.13 (m, 1H), 7.56–7.63 (m, 2H), 7.73–7.74 (m, 1H), 7.77–7.80 (m, 3H), 10.01 (s, 1H), 11.07 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=118.9–140.6, 123.8, 161.9, 196.9. MS (EI):

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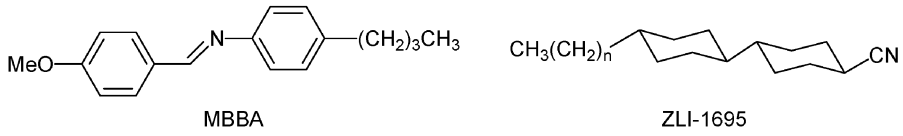


Scheme 1. Structures of the nematogens MBBA and ZLI-1695.

m/z: 267 $[M+1]^+$, 266 $[M]^+$, 220. **5b:** yield 82%, R_f=0.5 (chloroform), ^{1}H NMR δ=(500 MHz, $CDCl_3$): δ=7.05–7.06 (m, 1 H), 7.10–7.12 (m, 1H), 7.26–7.31 (m, 2H), 7.78–7.80 (m, 2H), 9.97 (s, 1H), 11.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=118.7–142.9, 161.4, 196.9, MS (EI): *m/z*=204 $[M]^+$. Elemental analysis: calcd (%) for $C_{11}H_8O_2S$, C 64.69, H 3.95; found, C 64.61, H 4.03.

2.1.2. Imines 6a and 6b (see scheme 3). A 100 ml two-necked flask equipped with a magnetic stirrer and a connection to the combined nitrogen/vacuum line was charged with (*R*)-**4** [7] (1.827 g, 6.315 mmol) and dry sodium sulfate (1.794 g, 12.63 mmol). The flask was closed with a septum, the air in the flask was replaced by nitrogen, and dry methanol (15 ml) and dry dichloromethane (15 ml) were added by syringes. The suspension was cooled to −20°C. Under vigorous stirring, a solution of the corresponding aldehyde **5a** or **5b** (6.631 mmol), dissolved under nitrogen in 30 ml of dry methanol or mixtures of methanol and dichloromethane, was slowly injected at such a rate that the temperature, monitored by a resistance thermometer, did not exceed −20°C. Stirring was continued at the same temperature for 48 h. The solid was then removed by filtration at 0°C and the filtrate concentrated in an oil pump vacuum at 0°C to give the imines **6a** and **6b**, respectively. The crude products were purified by stirring in *n*-pentane and subsequent filtration. They were stored at −18°C in a refrigerator.

(*R*)-**6a**: yield 98%, $[\alpha]_D^{20} = +125$ (*c*=1, chloroform), ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.89 (s, 1H), 5.55 (s, 1H), 6.99–7.00 (m, 1H), 7.10–7.13 (m, 1H), 7.16–7.18 (m, 7H), 7.23–7.24 (m, 1H), 7.33–7.37 (m, 5H), 7.48–7.55 (m, 3H), 7.61–7.65 (m, 3H) 7.71 (s, 1H), 8.40 (s, 1H), 12.97 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=79.1, 81.0, 118.2–145.1, 161.2, 167.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ=−63.07, MS (FAB, NBA): *m/z*=538 $[M+1]^+$, 355. (*R*)-**6b**: yield 94%, $[\alpha]_D^{20} = +161$ (*c*=1, chloroform), ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.80 (s, 1H), 5.46 (s, 1H), 6.83–6.85 (m, 1H), 6.94–6.96 (m, 1H), 7.02–7.16 (m, 11H), 7.25–7.29 (m, 5H), 7.44–7.45 (m, 1H), 7.53–7.54 (m, 2H), 8.29 (s, 1H), 12.82 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$): δ=79.1, 81.0, 118.0–145.1, 160.7, 167.5. MS (EI): *m/z*=475 $[M]^+$, 293, 188, 182.

2.1.3. Titanium complexes 1e and 1f (see scheme 3). A 50 ml two-necked flask was charged with the corresponding imine **6a** or **6b** (0.50 mmol); it was then equipped with a magnetic stirrer and a reflux condenser, connected to the combined nitrogen/vacuum line and closed with a septum. The air in the flask was replaced by nitrogen, the solid was dissolved by adding dry dichloromethane (10 ml), and titanium tetraisopropoxide (0.25 mmol) was injected under stirring at room temperature. The solution was stirred at room temperature for the time given below. The solvent was then removed in a rotary evaporator and the residue purified by column chromatography.

(A,R,R)-1e: This was prepared from (*R*)-**6a** (1.092 g, 2.031 mmol) and Ti(O*i*Pr)$_4$ (0.289 g, 1.016 mmol). The reaction mixture was stirred for 24 h. Yield: 0.720 g (63%), R_f=0.43 (*n*-hexane/chloroform, 1/2), $[\alpha]_D^{20} = +671$ (*c*=1, in chloroform), ^{1}H NMR (500 MHz, $CDCl_3$): δ=5.51 (d, *J*=8.7 Hz, 2H), 6.38 (s, 2H), 6.86–7.08 (m, 18H), 7.18–7.27 (m, 6H), 7.38–7.44 (m, 10H), 7.54–7.62 (m, 4H), 7.94 (d, *J*=7.3 Hz, 4H), 8.71 (s, 2H), ^{13}C NMR (125 MHz, $CDCl_3$): δ=87.7, 93.7, 119.8–147.1, 164.7, 166.9, ^{19}F NMR (470 MHz, $CDCl_3$): δ=−63.06, MS (MALDI): *m/z*=1119 $[M+1]^+$, 979, 936, 851, 807, 787, 755, 661. **(A,R,R)-1f**: This compound was prepared from (*R*)-**6b** (2.793 g, 5.873 mmol) and Ti(O*i*Pr)$_4$ (0.835 g, 2.937 mmol). The reaction mixture was stirred for 96 h. Yield: 2.182 g (75%), R_f=0.5 (*n*-hexane/chloroform, 1/3); $[\alpha]_D^{20} = +890$ (*c*=1, in chloroform), ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.49 (d, *J*=8.8 Hz, 2H), 6.41 (s, 2H), 6.88–7.17 (m, 25H), 7.28–7.34 (m, 5H), 7.42–7.48 (m, 6H), 7.96–8.01 (m, 4H), 8.70 (s, 2H), ^{13}C NMR (125 MHz, $CDCl_3$): δ=87.6, 93.5, 119.6–147.1, 164.4, 166.8, MS (FAB, NBA): *m/z* (%)=995 (15), $[M+1]^+$, 812 (55), 630 (94).

2.2. *Determination of HTP values and helicity*

The titanium complexes **1a**–**f** were dissolved in ZLI-1695 (Merck) at about 70°C with a mole fraction of 10^{-3} to 10^{-4}. The HTP values were determined by a modified Grandjean–Cano method [8, 9]. The induced chiral nematic phase was sandwiched between a glass plate and a plane convex lens. The rubbed surfaces of the glass plate and the lens were coated by polyimide (Merck). The radii of the disclination lines were observed with a polarizing microscope (Orthoplan Pol

Leitz) using an automatic registration with a videomicrographic system [8]. The sign of the HTP was determined from the colour change during the rotation of the azimuth of the polarizer in the microscope.

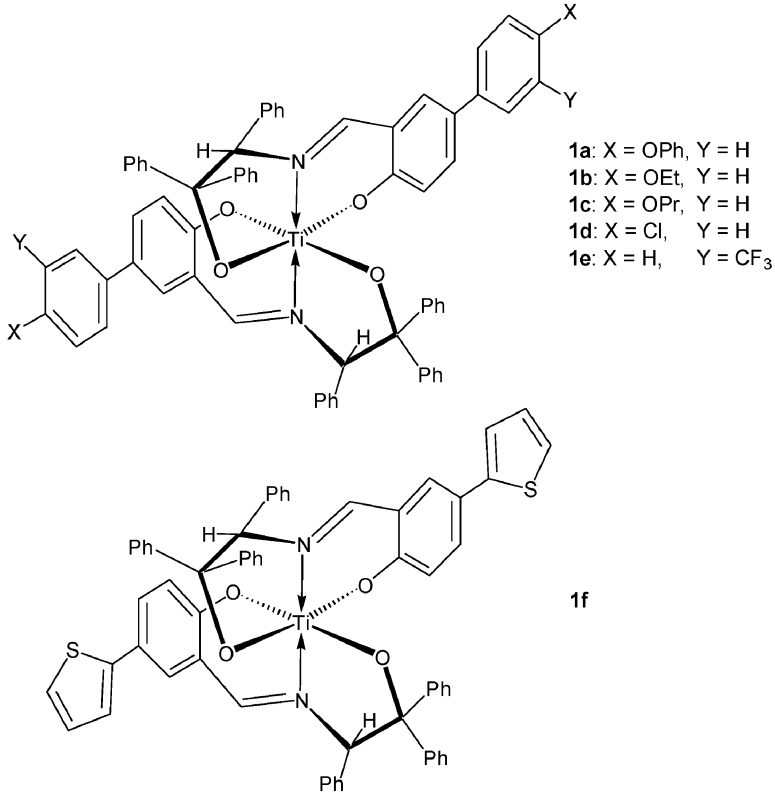
3. Results and discussion

A route to enantiomerically and diastereomerically pure imine-alkoxytitanium complexes has been opened recently [6, 10]. As shown by crystal structure analyses, the tridentade ligand is bound to the metal in a meridional arrangement, and the configuration has been determined to be (*A*,*R*,*R*) with respect to the chiral centres of the ligands (*R*) and the configuration of the titanium (*A*). The titanium complexes **1a**–**d** shown in scheme 2 have been described previously. They contain an arylphenoxy residue with different substituents in the *para*-biphenyl position. In order to investigate whether variations in this moiety will influence the HTP, the new complexes **1e** and **f** were synthesized in addition. They are substituted by the trifluoromethyl group and the heterocyclic thiophene moiety, respectively.

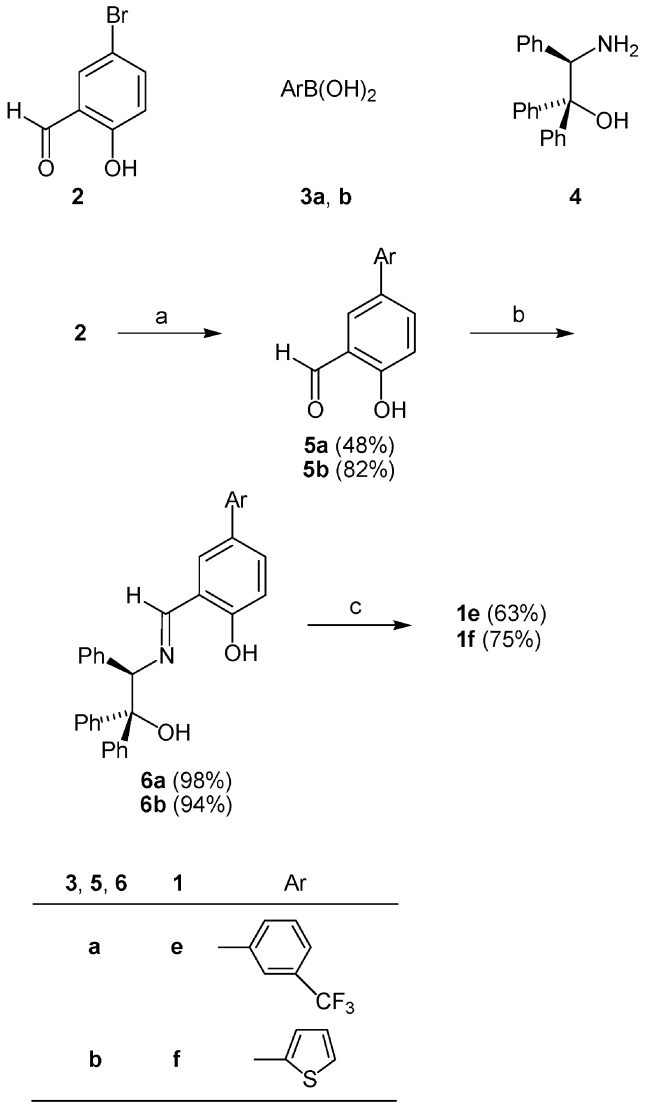
The synthesis of the titanium complexes **1e** and **1f**, shown in scheme 3, started with 5-bromo-2-hydroxybenzaldehyde (**2**) that was submitted to a Suzuki coupling reaction with the aromatic boronic acids **3a** and **3b** to give the biarylphenols **5a** and **5b**, respectively. Upon their condensation with (*R*)-amino alcohol **4** [7] the imines **6a** and **6b** result. When treated with titanium tetraisopropoxide in a molar ratio of 2/1, the complexes **1e** and **1f** are obtained in a highly diastereoselective manner. Their NMR spectra reveal that the (*A*,*R*,*R*)-configured products are formed as single isomers. The assignment of the absolute configuration is based on the CD spectra of the complexes **1e** and **1f** that display the same type of Cotton effects as the analogous compounds **1a**–**d**.

The HTP values of the complexes **1a**–**f** are shown in table 1. All the dopants in their (*A*,*R*,*R*) configuration induce a right-handed helix, indicated by a positive HTP value. The size of the HTP values depends on the particular substituents to a substantial degree if one takes into account the identical 'core unit' in all the titanium complexes **1a**–**f** that only differ in their 'periphery'. Derivatives with chlorine or trifluoromethyl substituents (entries 4 and 5) provided higher HTP values. Remarkably, the highest HTP value was obtained with the heterocyclic-substituted complex **1f**.

Addressing the question in which way the chirality transfer occurs from the dopants **1** to the nematic host, one has to take into account that the stereogenic centres



Scheme 2. Bis-chelated titanium complexes **1a**–**f** used as chiral dopants.



Scheme 3. Building blocks **2**–**4** and synthesis of titanium complexes **1e** and **1f**. Reagents and conditions: a) **3**, $Pd(dppf)Cl_2$ (5 mol%), Na_2CO_3, $MeOCH_2CH_2OMe$; 100°C, 5 h; b) **4**, Na_2SO_4, CH_2Cl_2, MeOH, −20°C; c) $Ti(OiPr)_4$ (50 mol%), CH_2Cl_2, rt.

Table 1. HTP values of titanium complexes **1a–f** in liquid crystalline phase ZLI-1695.

Entry	Titanium complex	HTP/μm^{-1}
1	**1a**	+63
2	**1b**	+76
3	**1c**	+83
4	**1d**	+101
5	**1e**	+115
6	**1f**	+131

(the metal and two carbon atoms) are located in the middle of the molecule. Therefore, any direct interaction of the stereogenic atoms with molecules of the nematic phase can be excluded. Due to the rigid structure of the complexes **1**, however, the chirality is transferred from the centre to the periphery, and the complete molecule adopts a chiral form. The long shape (i. e. the ratio of length to width) of the dopants **1**, that is caused mainly by the biaryl moieties, is also important to their interaction with the nematic phase. Molecules that feature a chiral form display a high anisotropy of the chirality transfer [2*a*]. The better the interaction along the long molecular axis through the biaryl moiety is with the molecules of the nematic phase, the stronger the chirality transfer is and the higher the HTP. This is best fulfilled by the thiophene-substituted complex **1f**. The chlorine and trifluoromethyl substituents in **1d** and **1e**, respectively, enlarge the axis and provide high HTP values also. At a glance, one would expect the phenolic ethers **1a**–**c** to have the same effect, because they also enhance the size of the molecule. It seems, however, that the elongated shape is disturbed due to the torsion of the ether bonds.

The HTP obtained in ZLI-1695 is lower than those determined in MBBA [6], a result that clearly underlines the strong dependence of the HTP on the particular structure of the nematic host. As the induction of HTP depends on non covalent bonding, it is plausible to assume that this type of interaction is much stronger between the aromatic moieties of the dopant and the aromatic rings of MBBA permitting π–π stacking and charge transfer forces. This type of interaction is impossible when the almost purely aliphatic and cycloaliphatic phase ZLI-1695 serves as the host. Nevertheless, the titanium complexes **1a**–**f** developed from the chiral amino alcohol **4** exhibit significant HTP even in the nematic compound ZLI-1695 [11].

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