Highly efficient chirality inducers in nematic liquid crystals: synthesis of 7,7′-disubstituted 2,2′-methylenedioxy-1,1′-binaphthyls

Christian Kühna,b, Matthias Bremera,b and Peter R. Schreinerb

aPerformance Materials - Liquid Crystals R&D, Merck KGaA, Darmstadt, Germany; bInstitute of Organic Chemistry, Justus Liebig University, Giessen, Germany

ABSTRACT

We report the synthesis of 7,7′-disubstituted 2,2′-methylenedioxy-1,1′-binaphthyls and demonstrate their application as chiral dopants in the nematic mixture MLC-6260 to produce highly twisted cholesteric phases. Especially mesogenic and/or polarizable groups in the 7,7′-positions of the bridged binaphthyls generate unusually high helical twisting powers.

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Liquid Crystals (LCs), or mesophases, are unique anisotropic materials. They form an intermediate state between the highly ordered crystalline solid and the isotropic liquid phase. Various liquid crystalline phases with different degrees of orientational order have been characterized [1]. Perhaps the most visible applications of LCs today are flat panel displays where the so-called nematic phase and its chiral variant, the cholesteric nematic phase (N*) are used. The latter was discovered in 1888 by Friedrich Reinitzer [2] when he studied derivatives of (chiral) cholesterol, but it can also be induced in achiral or racemic nematics by adding a suitable chiral dopant [3]. In addition to being used in displays, these induced cholesteric mesophases have numerous other applications, e.g. as polarizers [4], reflectors [5,6], and lasers [7]. Beyond these rather technical aspects, liquid crystal science over the last twenty years has significantly contributed to our understanding of mirror symmetry breaking in fluids and the emergence of chirality in general [8].

In nematic phases, the rod-shaped organic molecules are oriented in a parallel fashion along the so-called director and exhibit one-dimensional order. Through the addition of a small amount of chiral dopant (typically 1 mol%), the nematic phase is converted into a cholesteric phase, which is characterized by a helical structure. The ability of a chiral dopant to twist a nematic phase can be expressed by the helical twisting power \( \beta = \pm (pcr)^{-1} \), where \( p \) is the cholesteric pitch (rotation of the director by 360°), \( c \) the dopant molar fraction, and \( r \) its enantiomeric excess; the sign is taken positive for a right-handed (P) cholesteric phase and negative for a left-handed (M) one [9]. The nature of the chiral nematic phase is highly dependent on the molecular structure of the chiral dopant and the strength of the dopant/solvent interactions [10]. However, the design of efficient chiral dopants with high helical twisting power continues to be a challenge. Structure property-relationships are not straightforward [11,12], and the HTP theory is complicated [13–19].
Intra- and intermolecular effects such as hydrogen bonding [20] and photochemical control via cis-trans-isomerization of azobenzenes [21] have been shown to influence the stability of Blue Phases and the magnitude of the HTP, respectively.

The most extensively studied class of dopants are inherently chiral molecules, like binaphthyls, biphenyls, and helicenes [22]. 2,2'-Dihydroxy-1,1'-binaphthyl (BINOL) derivatives are already well-known for their efficient twisting properties in nematic phases. Especially bridged BINOL derivatives are strong chiral inducers, whereas small, unlinked substituents in the 2,2'-positions lead to low helical twisting powers [23,24]. In addition, the influence of various substituents in the 6,6'- and 7,7'-positions of bridged BINOL derivatives was investigated [25,26]. The introduction of aromatic and/or mesogenic moieties into specific positions of binaphthyl rings can generate excellent helical twisting powers [27,28], for example, BINOL derivatives with a variety of substituents in the 6,6'-positions have been studied [29]. We have now focused on bridged 7,7'-disubstituted derivatives to determine the influence of shape and electronic factors on cholesteric induction (Figure 1).

As substituents we chose polarizable aromatic, sterically demanding and mesogenic groups, as well as substituents with polarizable units. Compounds 17a–g were prepared from 2-naphthols derivatives 1a–c. The racemic products were separated by HPLC on a chiral column and their helical twisting powers measured in the nematic mixture MLC-6260 (Merck KGaA, Darmstadt, Germany). 7-Methoxy-2-naphthol 1a was converted into 7-methoxy-2-trifluoromethane-sulfonyloxy-naphthalene 2. Palladium-catalyzed cross-coupling [30] of trflate 2 with organoboranes 3a (commercially available) and 6 (obtained from the bromo compound) afforded 7-methoxy-2,2'-binaphthalene 4 and 2-(3,5-di-tert-butylphenyl)-7-methoxy-naphthalene 7. Finally, ether cleavage of 4 and 7 with boron tribromide gave the desired 7-substituted 2-naphthols 5a and 5b.

A suitable synthetic method for introducing an adamantyl moiety into an aromatic unit is by electrophilic aromatic substitution. It is known that the adamantylation of 2-naphthol leads to 6-adamantyl-2-naphthol [31]. Thus, we performed a reaction between 6-bromo-2-naphthol 1b and 1-adamantanol 8 in the presence of concentrated sulfuric acid and obtained 3-(1-adamantyl)-6-bromo-2-naphthol 9 in 45% yield [32]. Subsequently, 9 was treated with methyl iodide in the presence of potassium carbonate to protect the hydroxyl group, and the resulting 3-(1-adamantyl)-6-bromo-2-methoxynaphthalene 10 could be isolated in 58% yield. The bromo substituent was converted to a hydroxyl group in two synthetic steps. The palladium-catalyzed cross-coupling of 10 with bis(pinacolato) dibor on led to boronate ester 11 in 70% yield, which could be oxidized by oxone [33] (potassium peroxy monosulfate) to the desired 7-substituted 2-naphthol 5c. The additional naphthol derivatives 5d–g were prepared from 7-bromo-2-naphthol 1c, which is also commercially available but more expensive than 1a and 1c. Suzuki reaction of 1c with arylboronic acids 3b and 3c afforded the corresponding naphthols 5d and 5e in moderate yields. 1c was also coupled with the ethynylarenes 13 and 15, following the well-known Sonogashira protocol [34] affording the 7-substituted 2-naphthols 5f and 5g. The naphthol derivatives 5a–g were oxidatively coupled using a catalytic amount of CuCl(OH)-TMEDA (1 mol%) [35]. This reliable method afforded the desired 7,7'-disubstituted binaphthols 16a–g in moderate to good yields. Finally, the oxygen atoms of 16a–g were linked by one methylene bridge to produce rigid structures with suitable dihedral angles [36,37]. To this end the derivatives 16a–g were converted to the cyclic BINOLS 17a–g using an excess of diiodomethane and K$_2$CO$_3$.

**Figure 1.** (Colour online) Synthesis of 7,7'-disubstituted methylenedioxybridged binaphthyls (17a–g) from 2-naphthols 1a–c.
in acetone or dimethylformamide, with yields ranging from 50 to 77% (after column chromatography and recrystallization). To obtain 17a–g in optically pure form, we resolved the cyclized BINOLs into enantiomers by HPLC on a chiral stationary phase. The helical twisting powers were measured by the Grandjean-Cano method [38,39]. The values of β of enantiopure compounds 17a–g are collected in Table 1. With the separated enantiomers in hand, we investigated the cholesteric induction of 7,7ʹ-disubstituted 2,2ʹ-methylenedioxy-1,1ʹ-binaphthyls (17a–g) in the nematic mixture MLC-6260. Obviously, there are two factors that influence the helical twisting power: First, ring closure and second, the effect of the 7,7ʹ-substituents. The former is known and well-studied [23,24,36,37], while the latter has not yet been intensively investigated. However, the effect of the 7,7ʹ-substituents is even more impressive.

The trend of β values observed in MLC-6260 can be explained based on steric hindrance, dopant/solvent interaction and polarizability. Whereas flat aromatic groups (17a and 17d) increase the twisting power by 60% in relation to the unsubstituted compound 18, bulky groups (17b and 17c) show the opposite effect.

A remarkable helical twisting power of 102 µm⁻¹ was generated by compound 17e possessing mesogenic...
groups in the 7,7′-positions. This high β value could even be enhanced by introducing polarizable ethynyl units (β (17f) = 114 µm⁻¹). However, highly polarizable 4-ethynyl-thioanisole groups with a lower mesogenic character (17g) produce a moderate helical twisting power. Because of the promising results and the fact that polarizability plays a key role in intermolecular forces [40], we have investigated the influence of polarizability on the helical twisting power. Molecular polarizability tensors of BINOLs with low conformational flexibility were computed by using density functional theory (DFT).

The computations were performed with Gaussian09 [41] using molecular geometries optimized at the B3LYP level with the 6-31G(d) basis set (Table 1). Assuming that the interaction between dopant and solvent occurs in the xz-plane, we focussed on the polarizability tensors αₓₓ and αₜₜ. When looking at these polarizabilities, we found that BINOLs with a high polarizability in z-direction and low polarizability in x-direction generate high β values. This correlation is reasonable, especially for 17a and 17d with high polarizable groups in the 7,7′-positions (Figure 2). Deviations occur when groups are bulky or are

| BINOL | R       | R'     | Y    | β [µm⁻¹] | αₓₓ [a.u.] | αₜₜ [a.u.] | αₓₓ - αₜₜ [a.u.] |
|-------|---------|--------|------|---------|------------|------------|-----------------|
| 17a   | 2-Naph  | OCH₃O  | H    | 65      | 451.5      | 591.8      | 176.3           |
| 17b   | t-(Bu)₂Ph | OCH₃O  | H    | 3       | 525.2      | 620.9      | 95.7            |
| 17c   | Ad      | OCH₃O  | OMe  | 14      | 443.6      | 507.2      | 63.6            |
| 17d   | 9-Phen  | OCH₃O  | H    | 63      | 482.3      | 698.5      | 216.2           |
| 17e   | PhCyC₆H₄ | OCH₃O  | H    | 102     | n.d.       | n.d.       | -               |
| 17f   | CCPhCyC₆H₄ | OCH₃O  | H    | 114     | n.d.       | n.d.       | -               |
| 17g   | CCPhSMe | OCH₃O  | H    | 56      | 466.5      | 760.4      | 293.9           |
| 18a   | H       | OCH₃O  | H    | 41      | 127.9      | 264.3      | 136.4           |
| 18b   | H       | OCF₃O  | H    | 35      | 125.9      | 263.7      | 137.9           |
| 19a   | H       | OMe    | H    | 4       | 283.6      | 235.5      | 48.1            |
| 19b   | H       | OCF₂F₂ | H    | 7       | 262.6      | 284.6      | 22.0            |

(a) Resolution of racemic BINOLs into enantiomers was achieved by chiral SFC/HPLC.  
(b) The sign of β was not taken into account.  
(c) In atomic units (a.u.) from B3LYP/6-31G(d) computations with Gaussian09.  
(d) Reaction from (5)-BINOL.  
(e) MLC-6260 data. n.d. = not determined.

Figure 2. (Colour online) Proposed model for the chirality transfer from the 7,7′-disubstituted binaphthyl to the biphenyl-type solvent (HG = head group, FG = flexible group) and correlation between polarizability in the xz-plane and helical twisting power.
pointing away from the z-axis. Thus, polarizability seems to be a powerful parameter controlling the value of helical twisting power. Based on these results, we propose a simple model for the interaction between a chiral binaphthyl dopant and an achiral rod-shaped LC host-molecule such as the biphenyl shown in Figure 2. In this model, the solvent molecules ‘feel’ the polarizability and structural similarity of the chiral dopant. The chiral BINOL derivatives and LC molecules are associated through dipolar and dispersive interactions, but not with their biaryl axes in parallel alignment. We rather assume that the biphenyl axis of the solvent is aligned along the 7- and 7’-substituents of the chiral binaphthyl.

Furthermore, we suppose that the given helical section of the 7,7’-disubstituted binaphthyl is responsible for the strong chiral induction. The bridged binaphthyl core plays the role of a rigid and chiral scaffold that holds two twisted mesogenic moieties in place which then interact with host molecules and transfer the chirality to the bulk phase in a highly efficient manner.

In conclusion, we have shown that 2,2’-methylenedioxy-1,1’-binaphthyls with mesogenic and/or polarizable groups in the 7,7’-positions are excellent chiral inducers in the nematic mixture MLC-6260. Our investigation confirms that the helical twisting power depends both on the molecular shape and on the polarizability of the 7,7’-substituents.

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Matthias Bremer (http://orcid.org/0000-0003-3615-8953)
Peter R. Schreiner (http://orcid.org/0000-0002-3608-5515)

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