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New 6,6'-disubstituted-binaphthol derivatives as chiral dopants: Synthesis and temperature dependence of molecular conformations

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New 6,6'-disubstituted-binaphthol derivatives as chiral dopants: Synthesis and temperature dependence of molecular conformations

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A number of new chiral binaphthol (BN) derivatives with different substituents R,R' in the 6,6'-positions in open (BN-diethylethers) and bridged forms (BN-acetals) have been synthesized. The syntheses of the chiral 6,6'-disubstituted-2,2'-diethoxy-1,1'-binaphthyls (R,R' = -CH=CHCHO, -CH=CH-(*p*-BrPh), -CH=CH-(*p*-CHOPh)) and the chiral 9,14-disubstituted-dinaphtho[2,1-d:1',2'-f][1,3]dioxepins with R,R' = -CH=CH-(*p*-BrPh), -CH=CH-(*p*-CHOPh) are reported for the first time. The possible liquid crystalline properties and molar twisting powers (β_M) in three different nematic liquid crystals (LCs) of the BN derivatives were investigated. Derivatives with spatially extended substituents in the 6,6'-positions (e.g. styryl or vinyl) show unusually high molar twisting power (up to $124.5 \mu\text{m}^{-1}$). A direct correlation between the magnitude of β_M and the length of the substituents was found. Bridged forms, in which the dihedral angle θ between the naphthyl moieties is $\approx 54^\circ$, show higher twisting power than the corresponding open forms, where θ is allowed to vary around 90° resulting in an equilibrium between *transoid* and *cisoid* forms. From the different temperature dependencies of β_M of the open and bridged BNs, a molecular model was developed relating the molecular conformation and twisting power. Although no mesophase was found in any of the compounds synthesized, they can be considered as important precursors for the synthesis of potential chiral BN-containing LCs.

1. Introduction

Chirality has become one of the most important and complex topics of liquid crystal research today [1, 2]. The existence of many mesophases is due to chirality; examples include cholesteric or twisted nematic mesophases, blue phases [3, 4] and twist grain boundary (TGB) phases [5, 6]. The origin of chirality is usually an asymmetric atom, e.g. a carbon atom with four different substituents. Another source of chirality originates from hindered rotation about single bonds which leads to two conformationally stable optical antipodes (atropisomers). Whereas compounds with a chiral carbon atom have been well investigated in the area of liquid crystals, little attention has been paid to the chirality due to atropisomerism. Two examples of atropisomerism are the binaphthalene/binaphthol (BN)

derivatives in which chirality originates from the hindered torsional rotation about the 1,1'-C-C bond between the two naphthyl/naphthol moieties (figure 1).

An attempt to synthesise liquid crystals based on twisted binaphthol (BN) derivatives (figure 1) with a variety of substituents in different positions was recently described by Bhatt *et al.* [7]. No mesophases were observed in any of the BN-derivatives synthesized. 4,4'-Biphenanthryl derivatives which also have a highly twisted molecular structure, were found to exist in a liquid crystalline state [8, 9], but it has been shown that optically active BN-derivatives do possess high twisting power β in nematic liquid crystals. A variety of BN-derivatives with different substituents in the 2,2'-positions but without any substituents in the 6,6'-positions was studied [7, 10-13] for their use as chiral dopants producing twisted nematics at room temperature. It was shown that bridged (type b) compounds

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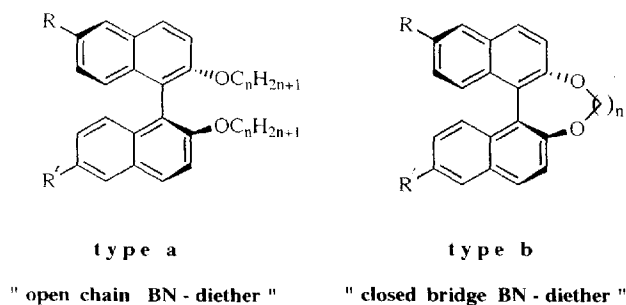


Figure 1. Open chain binaphthol-diethers (type a) and closed bridge binaphthol-diethers (type b) with substituents R,R' in the 6,6'-positions. The angle θ is defined as the dihedral angle between the naphthol moieties (*cisoid* $\theta < 90^\circ$, *transoid* $\theta > 90^\circ$).

have a high twisting power, whereas open-chain BN-derivatives (type a) have smaller values of twisting power. In the work of Heppke *et al.*, open-chain BN-derivatives were used as chiral dopants in order to obtain new blue phases [14, 15]. They were found to show decreasing twisting power with increasing temperature, but no explanation for this behaviour was given. Furthermore, BNs as dopants in liquid crystals were photo-racemized inducing a cholesteric to compensated nematic transition [16]. Even the use of BN-derivatives as LC-photo-triggers by photo-epimerization has been discussed [17]. As chiral dopants are used extensively in mixtures with nematic hosts for electro-optic device applications, BN-derivatives have also attracted attention in that field [18].

The dihedral angle between two naphthyl moieties of some binaphthyl derivatives was estimated with the help of both theoretical and experimental methods. In a number of investigations [10, 19–22], the dihedral angle θ between the two naphthalene moieties was determined from crystallographic data. For example, in 1,1'-binaphthyl crystals, the angle between the two naphthalene moieties was $\theta = 103^\circ$ in the optically active and $\theta = 68^\circ$ in the racemic crystal [20]. The calculated twist angle in the MM2' approximation was found to be $\theta = 78^\circ$, which is close to the angle in the racemic crystal, taking into account that the conformation obtained from the solid state will be influenced by packing effects. The calculated internal potential given by MM2' is very shallow in the region where the twist angle is between $\theta = 50^\circ$ and 130° , showing that this molecule can twist very easily in this region by weak intramolecular interaction [23]. Similar results were obtained by semi-empirical methods giving nearly perpendicular arrangements of the π -systems [24]. However, the combined results of fluorescence analysis in solution and of semi-empirical calculations on the isolated molecule showed that 2,2'-binaphthyl exists at room temperature as a

mixture of comparable amounts of two rotamers, a *trans*-like form with $\theta = 145^\circ$ and a *cis*-like form with $\theta = 35^\circ$ [25].

It was noticed [10] that there is a strong correlation between the twisting power and the value of the torsional angle (θ). According to [10] the maximum twisting power is expected when the dihedral angle between the naphthalene moieties $\theta = 45^\circ$ (or 135°), and the minimum twisting power is expected when $\theta = 90^\circ$ (or 0°). Moreover, *cisoid* ($\theta < 90^\circ$) or *transoid* ($\theta > 90^\circ$) conformations of BN compounds could be deduced by the sign of the twisting power (positive for a right-handed cholesteric and negative for a left-handed one) [11, 12, 26].

These previously reported results indicate that the difference of twisting power observed for bridged and unbridged BNs and the lack of ability to form mesophases are connected with the molecular structure, primarily with the torsional angle between the naphthyl moieties. A decrease of the torsional angle leads to flattening of the molecule. This should stimulate the appearance of the liquid crystal state in pure BN-systems and prevent the formation of a cholesteric mesophase in a nematic matrix when using BNs as dopants, since chirality vanishes for a flat shape of the BN-molecule.

In order to investigate these findings further we have synthesized a series of optically pure BNs in which the substituents in the 6,6'-positions are varied in a systematic way (different length and polarity), allowing a correlation between twisting power β and molecular shape to be revealed. By synthesizing both open chain BN-diethers (type a, $n = 2$) and closed-bridge BN-acetals (type b, $n = 1$) with a flat molecular structure, the effect of molecular conformation elucidated by measurements of the temperature dependence of twisting power β has been addressed. The possible existence of a liquid crystal state of the new compounds was tested.

2. Synthesis

The starting compound for all the synthetic routes was optically pure (*R*)- or (*S*)-1,1'-bi-2-naphthol **1** (optical purity > 0.99) which was prepared according to Kazlauskas [27]. As strongly acidic or basic conditions, especially in combination with heat, favour the racemization of BN-derivatives [28], appropriately mild reaction conditions, which ensure retaining enantiomeric purity during synthetic transformations, were chosen. The syntheses of **2**, **3a**, **4a** and **4b** have been reported earlier [29, 30]. **3b** was obtained by alkylation of **1** with dibromomethane in boiling acetone using K_2CO_3 as base. This was found to be superior to the method described earlier [16] (figure 2).

The aldehydes **5a** and **5b** were prepared according to

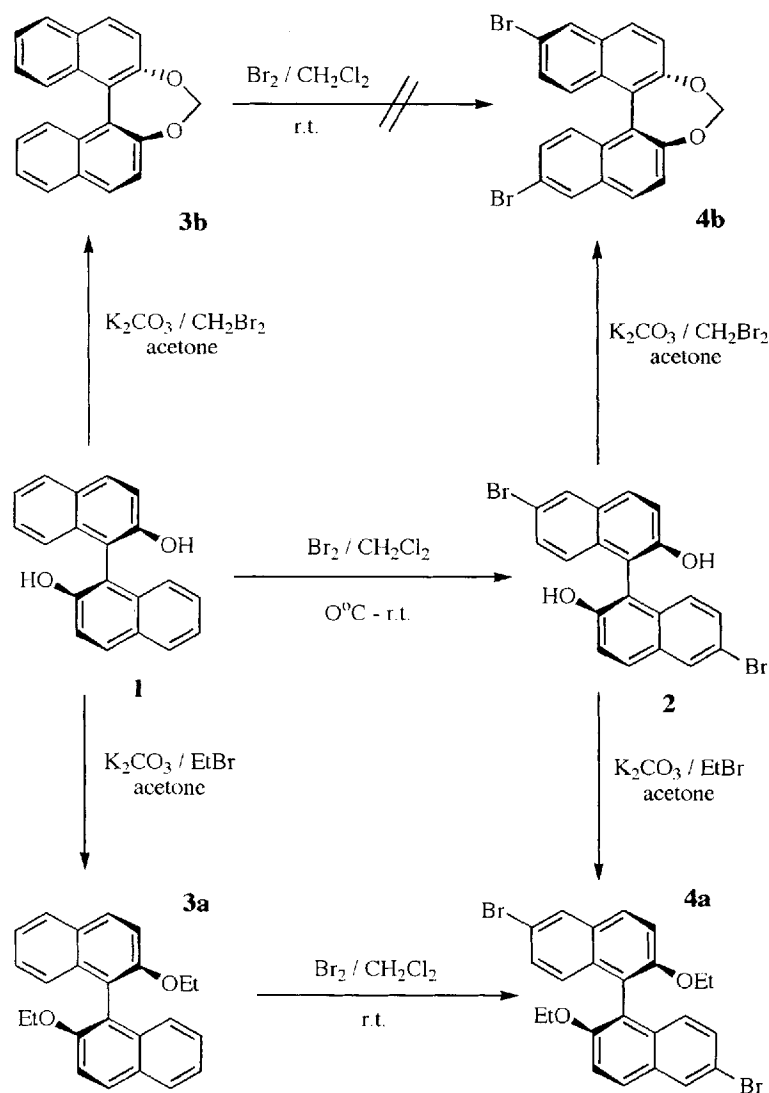


Figure 2. Synthetic scheme for compounds **4a** and **4b**.

a known procedure [30]. Syntheses of the vinyllogous aldehydes **6a** and **6b** were performed using diethyl 2-(cyclohexylamino)vinylphosphonate [31] in a Horner–Emmons reaction followed by acidic hydrolysis of the imines, giving the pure compounds after chromatography [30] (figures 3 and 4).

Reaction of **5a** and **5b** with diethyl (4-bromobenzyl)phosphonate [32] in a Horner–Emmons reaction in dimethoxyethane at room temperature, using sodium hydride as base, gave the BN-stilbenes **7a** and **7b**. The yields of crude products were almost quantitative and they could be used without further purification in the next step. Lithiation of the BN-stilbene-bromides **7a** and **7b** using *n*-BuLi in THF at -78°C and subsequent

reaction with *N,N*-dimethylformamide gave the BN-stilbene-aldehydes **8a** and **8b** after acidic hydrolysis. Column chromatography on silica was necessary in order to obtain the pure aldehydes.

The optical purity for compounds **3b–8b** was confirmed by the splitting of the signal for methylene protons due to diastereomeric interaction with a large excess of (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol (Aldrich) in $^1\text{H-NMR}$ experiments. These experiments indicate that racemization did not occur during the reaction conditions. This should also be the case for open chain BN-diethers (type a, $n=2$) because of the higher racemization energy [33]. This is consistent with the high specific rotation measured for all compounds synthesized.

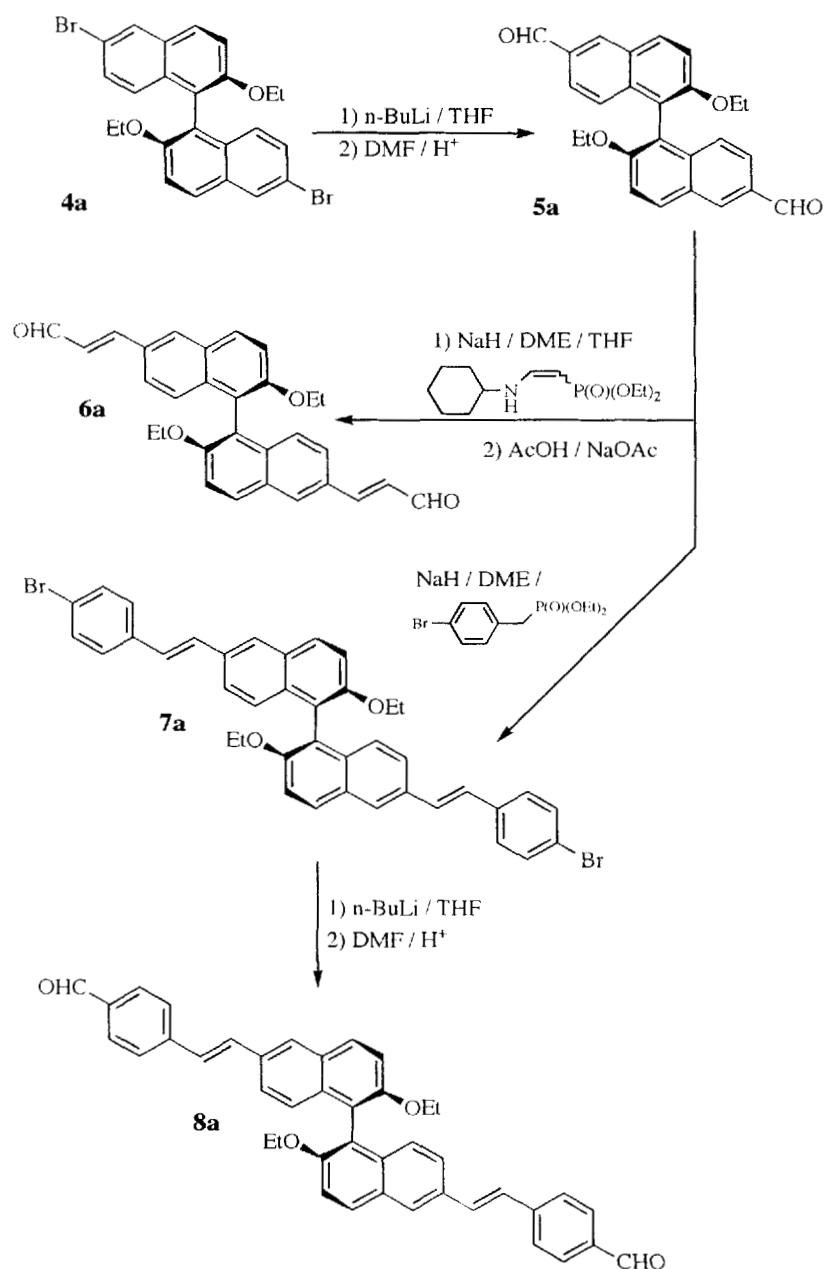


Figure 3. Synthetic scheme for compounds 5a–8a.

3. Results and discussion

The possible existence of liquid crystal properties for the BN-derivatives prepared was investigated by differential scanning calorimetry (DSC) and hot stage polarizing microscopy. No mesophases were found in any of the compounds. Many of them do not crystallize on cooling after melting, or only crystallize after a long period of time (weeks), indicating that a glassy state forms. In these cases the typical glass transition peak was found on the DSC scans.

Twisting power measurements were carried out by the

droplet method in a glycerol matrix [34] in the temperature interval 20–70°C for three different commercially available nematic mixtures: LC 1277 (alkyl- and alkoxy-cyanobiphenyls, NIOPIK, Russia), LC 1630 (alkylpyrimidines and cyanobiphenyls, NIOPIK, Russia), and LC ZLI-1695 (non-polar mixture for UV–VIS spectroscopy of unknown composition, E. Merck). Additionally the Grandjean–Cano [35,36] method was used in several cases in order to verify the results obtained by the droplet method. Both methods gave similar results with a variation of less than 15%. For high concentrations

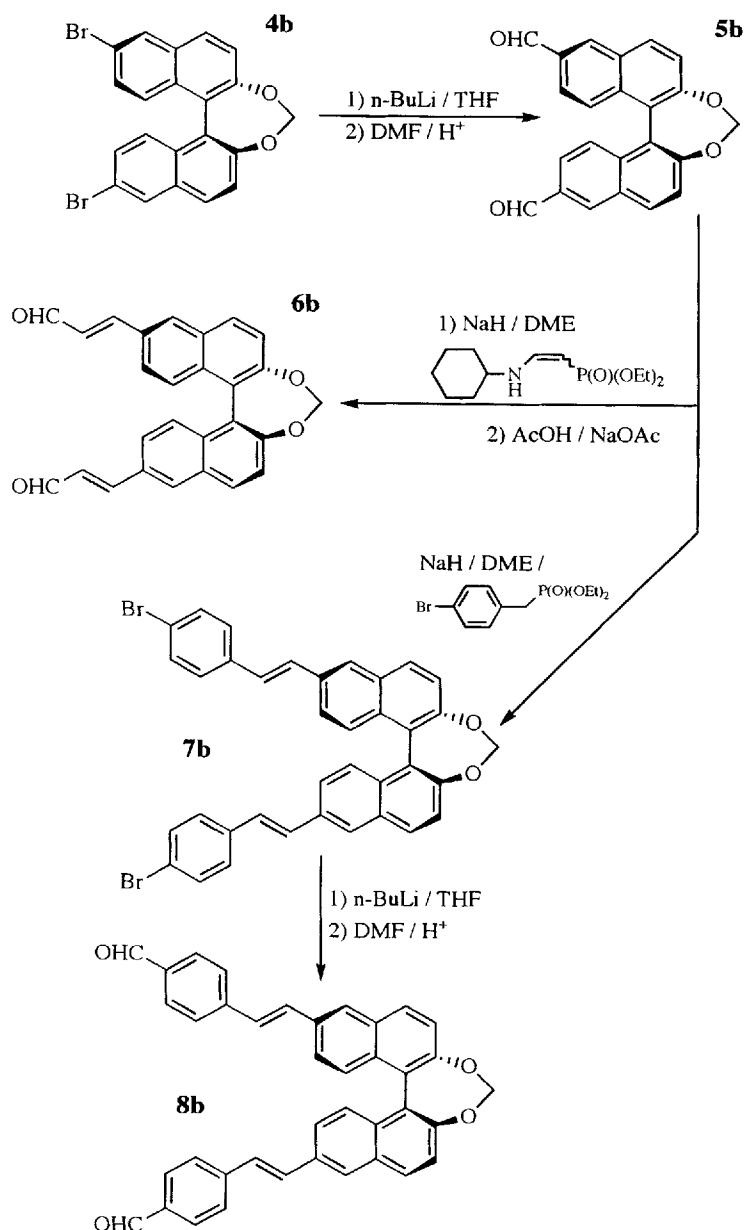


Figure 4. Synthetic scheme for compounds **5b–8b**.

of chiral dopant **4b**, coloured cholesterics were obtained. In this case the pitch was additionally determined by selective reflection measurements. The handednesses of the helices were determined by comparison with cholesteric phases of known helical sense or by the Heppke–Oestreicher method [33, 37]. For low concentrations (<4 mass per cent), the helical pitch showed a linear variation with concentration for all chiral dopants. For higher concentrations (>4 mass per cent) the pitch slightly decreased and then tended to saturate before the solubility limit of the dopant was reached. Table 1 collects data for the helicity and molar twisting power

of compounds **1–8a/8b** dissolved in the three nematic solvents at different temperatures for low concentrations (<4 mass per cent), within the linear range.

It can be seen that the twisting powers of the BN-acetals (type b, $n=1$) exceed significantly those of the open chain compounds (type a, $n=2$) with the same substituents in the 6,6' positions for a given temperature. This difference is especially significant in the case of the ZLI-1695 nematic host, where the twisting power of the open chain derivatives (type a) was sometimes too small to be measured. A second correlation exists between the twisting power and the length of the substituents in the

Table 1. Helicity of (S)-enantiomers (M denotes a left-handed and P a right-handed cholesteric; ^a specifies the cases in which the determination was carried out on the (R)-enantiomer) and molar twisting power β_M (μm^{-1}) at different temperatures in the different nematic hosts: (a) NIOPIK LC 1277, (b) NIOPIK LC 1630, and (c) MERCK LC ZLI-1695.

(a)

Compound	Helicity	Temperature/ $^{\circ}\text{C}$						
		20	30	35	45	55	60	65
1 ^a	P	9.0	—	5.5	5.0	—	—	—
2	P	15.5	—	13.0	11.5	11.0	10.5	11.0
3a	M	10.0	—	9.0	7.5	6.5	6.0	6.0
3b	P	41.5	—	38.5	37.0	38.0	40.0	—
4a	M	19.0	16.0	15.0	14.0	13.0	12.5	—
4b	P	57.0	56.0	57.0	56.0	55.5	57.0	—
5a	M	20.0	—	19.0	15.0	13.0	11.5	9.5
5b	P	—	56.0	—	58.5	54.0	53.0	52.0
6a ^a	M	—	34.0	—	27.0	24.0	22.0	18.5
6b	P	—	78.0	—	78.5	79.0	80.0	75.0
7a ^a	M	51.0	—	46.0	37.5	34.0	32.0	26.5
7b	P	115.0	—	124.5	108.5	108.5	108.5	105.5
8a ^a	M	—	40.5	—	32.0	26.0	23.5	18.5
8b	P	—	95.0	—	91.0	91.0	94.0	86.0

(b)

Compound	Helicity	Temperature/ $^{\circ}\text{C}$						
		20	35	45	55	60	65	70
1 ^a	P	12.5	9.5	6.0	10.5	10.0	8.5	7.5
2	P	21.5	20.5	20.5	18.0	15.0	13.0	12.0
3a	M	4.5	4.0	4.0	3.0	3.0	2.5	2.5
3b	P	30.5	31.0	32.0	30.0	29.0	—	—
4a	M	16.0	16.0	15.0	13.0	12.0	11.0	11.0
4b	P	40.5	40.0	39.0	40.5	40.0	39.0	40.5
5a	M	19.0	17.0	17.0	14.0	13.0	12.5	—
5b	P	—	21.0	21.0	21.0	20.0	—	—
6a ^a	M	—	30.0	26.5	26.0	24.0	21.3	19.0
6b	P	—	61.0	59.0	58.5	59.0	57.5	54.0
7a ^a	M	48.5	45.0	43.0	38.0	35.0	34.0	33.5
7b	P	95.5	90.0	88.5	87.0	95.5	84.0	81.0
8a ^a	M	—	23.0	21.5	20.0	16.0	16.5	13.5
8b	P	—	77.5	76.5	73.5	74.5	73.5	72.0

(c)

Compound	Helicity	Temperature/ $^{\circ}\text{C}$					
		30	45	55	60	65	70
3a	—	1.0	1.0	1.0	1.5	1.5	—
3b	P	21.5	25.0	—	—	—	—
4b	P	19.0	20.0	—	—	—	—
5a	P	1.0	1.0	1.0	1.0	1.0	—
5b	P	41.5	43.0	41.5	43.5	43.0	—
6b	P	32.0	33.5	34.0	35.0	35.0	35.0
7b	P	84.0	94.0	90.5	93.5	91.5	93.5
8a	P	10.0	12.5	14.0	15.0	15.0	17.0

6,6'-positions. The length of the guest (dopant) correlates directly with the magnitude of twisting power (see also figure 6). This may result from increasing dipole–quadrupole interactions between the guest molecules and the surrounding nematic phase.

It has been shown that the addition of a non-mesogenic guest molecule to a liquid crystal matrix changes the range of the mesophase of the nematic mixture, resulting in either a decrease or an increase in the clearing temperature in comparison to the clearing temperature of the pure liquid crystal [38]. The change of the nematic–isotropic transition temperature is dependent on the size and shape of the guest molecule and on the guest molecule's concentration, as well as on the mutual intermolecular interactions among the guest and host molecules. The change indicates the destabilization or stabilization of the nematic host by the guest molecules [38, 39]. The cholesteric–isotropic transition temperatures for some of the chiral dopants in the nematic hosts LC 1277 and LC 1630 are illustrated in figures 5(a) and 5(b). The tendency found in all three hosts for all chiral dopants is that open chain BN-diethers (type a, $n=2$) disturb the mesophase more significantly than BN-acetals (type b, $n=1$). The most considerable change can be observed for **5a** and **6a**. It can furthermore be seen that increasing the length of the substituents in the 6,6'-positions leads to a decrease of the cholesteric–isotropic transition temperature. The stilbenc-BN derivatives, however, do not follow these tendencies strongly, as their elongated shape (width to length ratio) is closer to the shape of their host.

The lower twisting power and higher disturbing influence of the open chain BN-diethers (type a, $n=2$) in comparison with those of the bridged BN-acetals (type b, $n=1$) in the three hosts correlates well with their molecular structures. The small twisting angle of bridged BN-derivatives was found to be 47° by PM3-calculations for all derivatives independent of the substituents in the 6,6'-positions, allowing them to interact with the nematic matrix more efficiently. This leads, in accordance with Gottarelli [11], to a high twisting power. The high dihedral angle of the open chain compounds ($\theta=90^\circ$ according to PM3-calculations) leads to a destabilisation of the matrix and is manifested in a decrease of twisting power in comparison with the bridged BN-acetals.

In the nematic mixtures LC-1277 and LC-1630, the temperature increase leads to a decrease of twisting power both for open-chain (type a, $n=2$) and bridged (type b, $n=1$) BNs, but for the open-chain BNs the changes are much more significant. This behaviour is illustrated in figure 6 for some of the compounds in LC 1277. In LC-ZLI-1695, the behaviour of the twisting power with increasing temperature is different: the pitch

of open-chain BN-diether **8a** decreases, whereas the pitches of the bridged BNs are practically constant.

It is possible to determine the preferred conformation (*cisoid* or *transoid*) of open-chain BN-derivatives (type a) by using experimental data concerning handedness, together with knowledge of the absolute configuration. For the (*S*)-configuration, a right-handed cholesteric indicates a *cisoid* molecular conformation and a left-handed cholesteric corresponds to *transoid* [12]. On the basis of our data (tables 1(a) and (b)), the conformations of open-chain molecules **3a–8a** were determined as *transoid* and all conformations of bridged molecules were determined as *cisoid* in LC 1277 and LC 1630 hosts. For compound **4a**, this is in accordance with the structure in the solid state, where the dihedral angle θ was recently found to be 119° [22], still bearing in mind that the conformation in the crystal is influenced by packing effects. The open chain compounds **1** and **2** prefer a *cisoid* conformation in LC 1277 and LC 1630 hosts, a fact which was earlier attributed to hydrogen bonding [12]. The preferred conformations of **5a** and **8a** in the non-polar ZLI-1695 LC-mixture were found to be *cisoid* (table 1(c)).

The significant changes in pitch during heating can be explained in terms of changes of molecular conformation. To support this point of view, one should consider the behaviour of the potential energy of the molecules as a function of the dihedral angle between the two naphthalene moieties. For bridged binaphthol-acetals (type b, $n=1$) without substituents in the 6,6'-positions, the free energy of activation for racemization was found, from pitch changes in liquid crystals, to range from 33.2 to 33.4 kcal mol⁻¹ [33]. This prevents racemization in the temperature range of the twisting power measurements. Free rotation around the C₁–C₁ bond is restricted by the dioxymethylene bridge, and since possible deformations of the dihedral angle between the naphthyl moieties are not high, the geometry of the molecule should be determined mainly by the conformation of the heterocyclic ring. The potential energy curve should therefore have a rather sharp minimum at $\theta=54^\circ$ as shown by semi-empirical calculations and recently confirmed by X-ray diffraction [22]. For open chain BNs there are two possible mechanisms of racemization. They differ in the direction of rotation of the naphthalene moieties and, therefore, by the existence of *cisoid* and *transoid* states [40]. The existence of a pure *cis*-state is restricted by steric repulsion of the naphthalene hydrogen atoms in the 8,8'-positions and the substituents in the 2,2'-positions. The same is true for a pure *trans*-state leading to a free energy of activation for the racemization for 1,1'-bi-2-naphthol of 37.5 kcal mol⁻¹ [33]. Far from the pure *cis*- and *trans*-states there is freedom of rotation around the connecting C₁–C₁ bond which was

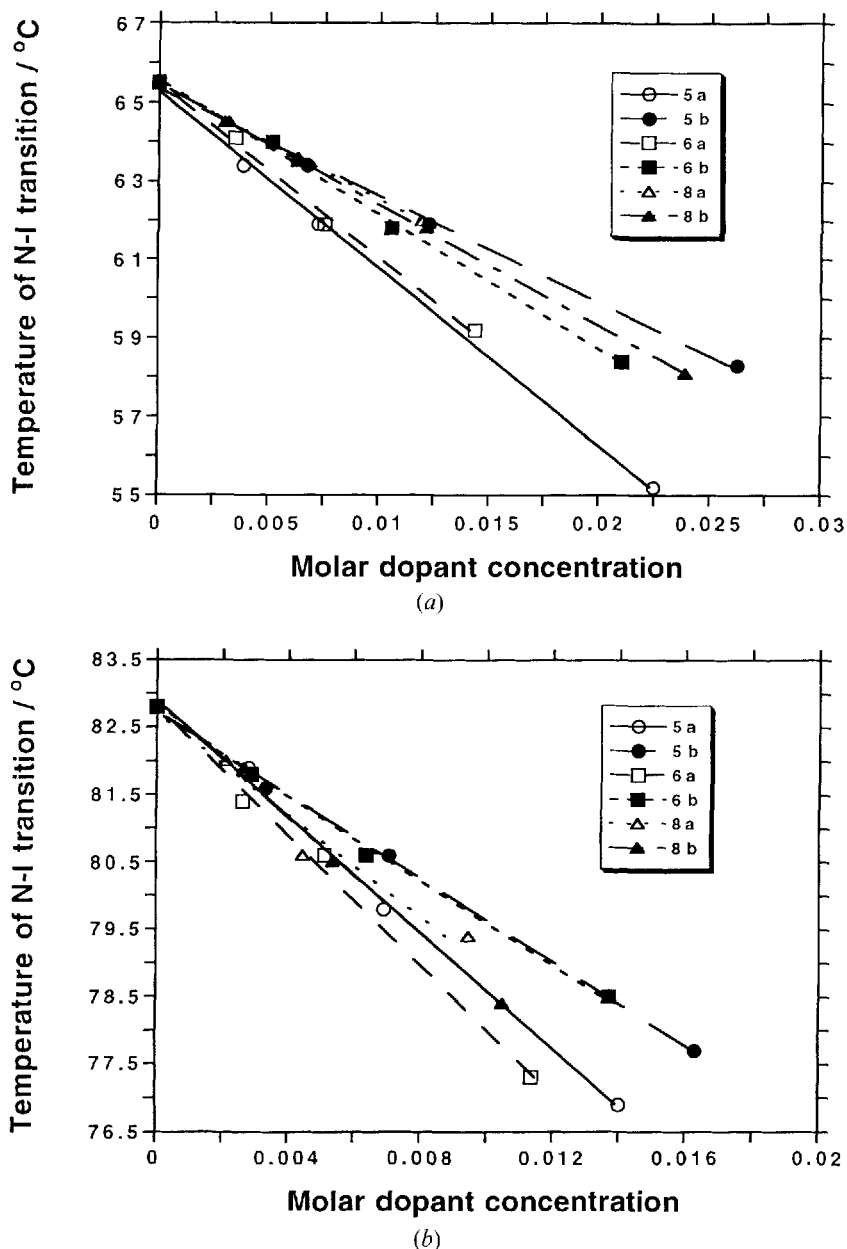


Figure 5. Nematic-isotropic transition temperature (initial temperature) of **5a**, **5b**, **6a**, **6b**, **8a**, and **8b** as a function of molar concentration (a) in LC 1277 (b) in LC 1630.

confirmed by several [23–25] theoretical studies showing the existence of a broad minimum in the potential curve around $\theta = 90^\circ$.

All these calculations were performed for *in vacuo* conditions, assuming that either all molecular fragments are fixed or all of them are not fixed during the search for the global minimum. In a liquid crystal matrix there are additional strong influences resulting from the surroundings of the guest molecule, differing significantly from the situation *in vacuo*. It is however difficult, if not

impossible, to take this influence into account. Nevertheless the nematic surroundings will freeze some molecular degrees of freedom and relax others. To simulate this effect we have calculated the energy of the molecules with different frozen fragments as a function of the torsional angle θ using the MM+ method. The MM+ results are presented in figure 7 for the open chain BN-diethyl ethers (i.e. **5a**).

The minimum of the intramolecular energy usually corresponds to an angle θ of 90° between the naphthyl

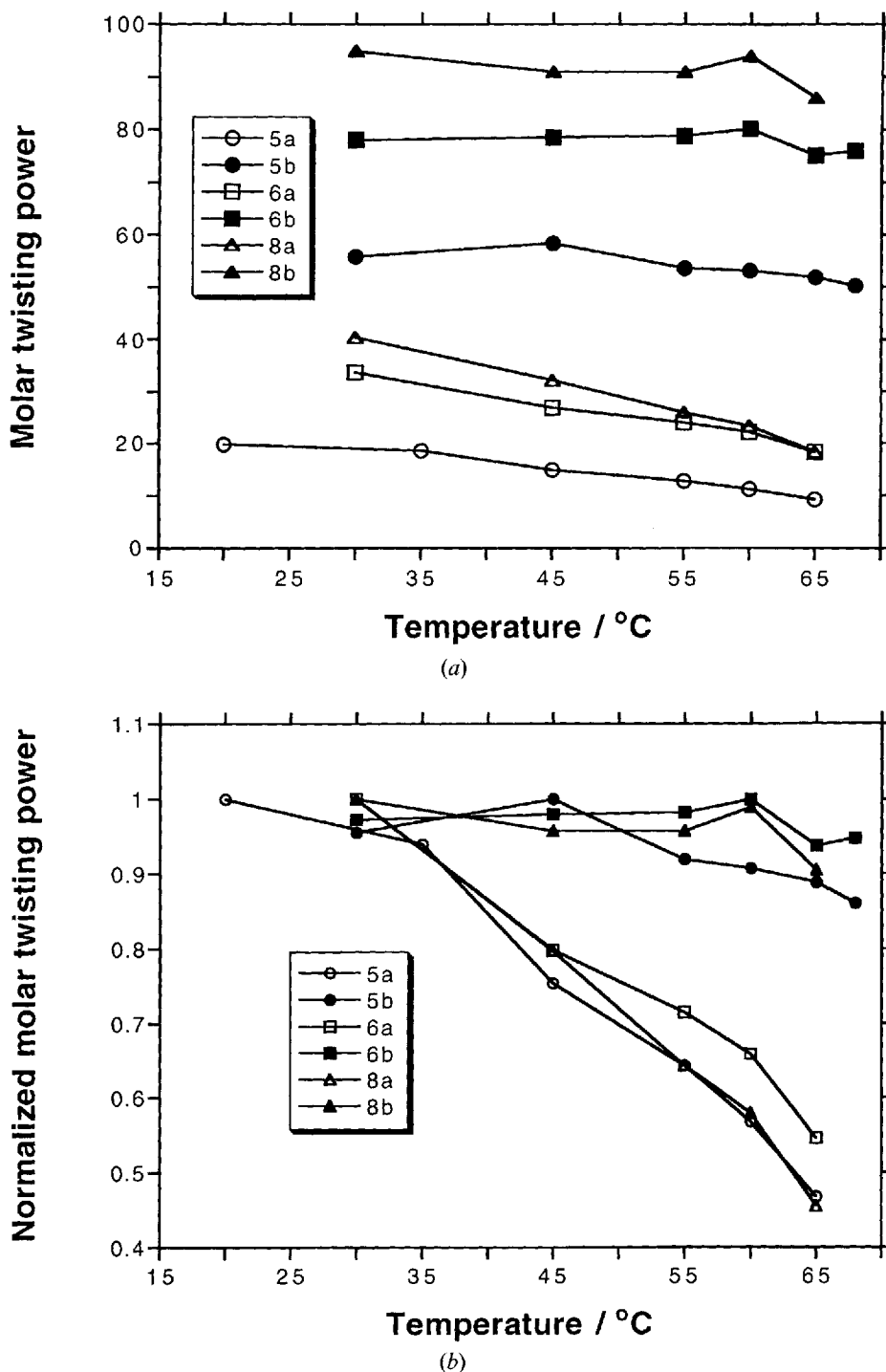


Figure 6. Absolute twisting power β_M (a) and normalized molar twisting power β_M (b) as functions of temperature in LC 1277.

moieties and it is important to note that the potential curve is asymmetric. The degree of this asymmetry depends on the number and nature of the molecular fragments to be fixed. For example, if we constrain the conformation of the alkyl chains, the potential curve is almost symmetrical. If we do not fix the geometry of the

alkyl chains and fix the geometry of the naphthyl rings instead, then the potential energy curve becomes asymmetrical as alkyl chains tend to pack far from each other. This asymmetry should be higher in a liquid crystal matrix than *in vacuo* because of the additional influence of the anisotropic molecular field. This is

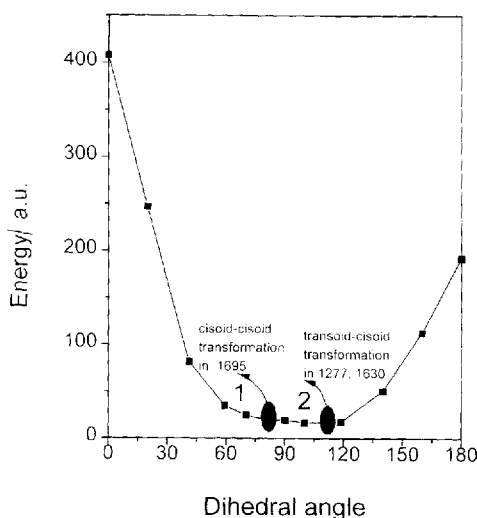


Figure 7. Scheme of the potential energy of open chain BN-diethers (type a) (calculated by MM+ for **5a**) as a function of the dihedral angle between the two naphthyl moieties. The initial average conformations of open chain BN-diethers and their possible transformations on heating in the nematic hosts are indicated: 1 = *cisoid-cisoid* transformations in LC ZLI-1695; 2 = *transoid-cisoid* transformation in LC 1277, LC 1630.

especially important in the case of molecules with large dipole moments resulting from the presence of acceptors in the 6,6'-positions [30]. Due to the strong dipole-dipole interactions in the polar nematics LC 1277 and LC 1630, *transoid* states of BNs should be energetically favoured for open chain molecules **3a-8a** in these hosts. As a result, the potential curve is distorted due to the dipole-dipole interactions leading to the existence of predominantly *transoid* states. In ZLI-1695 host, the situation is opposite with a preferred *cisoid* conformation. Thus, depending on the nature of the intermolecular interactions, the population of *transoid* states with $\theta > 90^\circ$ and *cisoid* states with $\theta < 90^\circ$ can differ significantly in accordance with the degree of asymmetry of the potential curve. Depending on this degree of asymmetry, the population of *transoid* states can grow relatively to the population of *cisoid* states or *vice versa*. This increase or decrease in the population of *transoid/cisoid* states starting from a given initial average conformation of **5a** is also illustrated in figure 7. Thus the molecular conformation can easily change during heating, which results in the observed change of twisting power.

The relationship between optical activity and the stereochemical conformation as a function of the dihedral angle between the molecular planes of aromatic moieties was investigated in [41] where a coupled oscillator model was proposed. It was shown theoretically for binaphthyl derivatives [42] and experimentally for BNs [43], that the magnitude of optical rotation at

a given wavelength is a function of the dihedral angle θ between the naphthyl moieties. The specific rotation of **4a** and **4b** in CHCl_3 was recorded as a function of temperature in the range of 0–55°C. The specific rotation of the closed acetal **4b** changes only a little (97% of initial value at 55°C), whereas the rotation of the open BN-diether **4a** decreases significantly on heating (54% of initial value at 55°C). The observed linear decreases of the specific rotation of **4a** can be attributed to changes in the populations of *transoid/cisoid* conformations according to the coupled oscillator model. The closed derivative only adopts minor geometrical changes on heating, due to steric hindrance caused by the strain of the heterocyclic ring. This leads to a constant magnitude of rotation as the dihedral angle between the two naphthyl moieties is fixed. Conformational changes of the BN-diethers (type a) should also occur in a liquid crystal host leading to the observed changes in the helical pitches.

Both the increase of twisting power of open chain BN-diethers in ZLI-1695 and the decrease in LC 1277 and LC 1630 with increasing temperature can be related to changes of the molecular conformations. In the ZLI-1695 mixture the angles between the naphthyl moieties of **8a** change on heating from an initial average *cisoid* distribution to an average *cisoid* distribution which is closer to the theoretically predicted dihedral angle of maximum twisting power $-\theta = 45^\circ$ [44]. In LC 1277 and LC 1630, the situation is different, as the initial preferred average distribution is *transoid*. As the twisting power decreases on temperature increase, the dihedral angle of the dopants **3a-8a** changes from *transoid* to *cisoid*. The differences in the directions of these changes can be explained by the physical properties (especially the polarity) of the different nematic hosts. As the total dipole moment of the BN-derivatives is a function of the dihedral angle, and the different host surroundings lead to different degrees of stabilization of the conformations, there should be a significant influence on the conformational distributions for different hosts, leading to different populations of *cisoid* and *transoid* states and thus different potential energy curve shapes.

4. Experimental

4.1. General

DSC scans were performed using a Mettler TA-4000. Polarizing microscopy was done with a Polam microscope from LOMO using a Mettler FP-85 hot stage. The average molecular masses of the liquid crystals were determined by gas chromatographic analysis/mass spectrometry using a Hewlett-Packard 5890 Series II instrument with a 5972 series detector, fitted with a 30 m \times 0.25 mm HP. 5 M. S. (0.25 μm , cross-linked 5% Ph Me Silicone) column: NIOPIK-LC 1277, MW =

288.9; NIOPIK-LC 1630, MW = 282.1; MERCK ZLI-1695, MW = 241.7. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-250 or a Varian Unity 400 as noted. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. UV-VIS spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. Mass spectra were recorded on a VG Masslab12-250 and on a Jeol JMS-HX/HX110A Tandem Mass Spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR1760X spectrometer. Elemental analyses were performed at the Microanalysis Laboratory at the University of Copenhagen. Melting points were measured on a Büchi apparatus or a homemade heating stage and are corrected. All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. THF was distilled under N_2 from Na/benzophenone, and DMF and DME were distilled from CaH_2 . Dry acetone was of HPLC grade as were all solvents used for spectrophotometry. K_2CO_3 and NaI were dried at 150°C for one week prior to use. Silica and TLC-plates were from Merck: Kieselgel 60, 0.063–0.200 mm, 70–230 mesh ASTM, and DC-Aluminiumfolien Kieselgel 60 F₂₅₄, d = 0.2 mm.

4.2. Synthesis

4.2.1. (S)-Dinaphtho[2,1-d:1',2'-f][1,3]dioxepin **3b**

A mixture of (S)-2,2'-dihydroxy-1,1'-binaphthyl **1** (10.00 g, 34.9 mmol), dibromomethane (12.13 g, 69.8 mmol), dry potassium carbonate (20.0 g) and a catalytic amount of NaI in dry acetone (50 ml) was stirred magnetically and heated under reflux until the reaction was judged to be complete as monitored by TLC (24 h). After cooling, the reaction mixture was poured into water and shaken $3 \times$ with CH_2Cl_2 . The combined organic phases were washed $2 \times$ with NaOH (10%), and $2 \times$ with water. After drying over MgSO_4 the solvent was removed *in vacuo* after filtration. The white powder obtained was recrystallized from heptane ($80\text{--}110^\circ\text{C}$), washed with light petroleum ether and dried in air. Yield 9.69 g (93%); m.p. $183\text{--}186^\circ\text{C}$, lit. [43] $182\text{--}184^\circ\text{C}$. Anal: calcd. for $\text{C}_{21}\text{H}_{14}\text{O}_2$ (298.34) C 84.54, H 4.73; found C 83.48, H 4.65 per cent. $^1\text{H-NMR}$ (CDCl_3) δ (400 MHz): 7.97 (d, $J = 8$ Hz, 2H), 7.93 (d, $J = 8$ Hz, 2H), 7.50 (br. d, $J = 9$ Hz, 2H), 7.47 (d, $J = 9$ Hz, 2H), 7.44 (ddd, $J = 8, 7, 1.3$ Hz, 2H), 7.30 (ddd, $J = 9, 7, 1.5$ Hz, 2H), 5.69 (s, $-\text{CH}_2-$, 2H). $^{13}\text{C-NMR}$ (CDCl_3) δ (100.6 MHz): 151.12, 132.05, 131.68, 130.19, 128.27, 126.79, 125.98, 125.93, 124.88, 120.82, 103.03. MS (FAB +): $m/z = 299$ (MH +). $[\alpha]_{\text{D}}^{25} = +737^\circ$ ($\text{CHCl}_3, c = 0.02$).

4.2.2. (R)-(E,E)-3,3'-(2,2'-Diethoxy-1,1'-binaphthyl-6,6'-diyl)dipropenal **6a**

Sodium hydride (610 mg, 20.32 mmol) was added in portions to a mixture of diethyl 2-(cyclohexylamino)-vinylphosphonate (84%) (4.72 g, 15.17 mmol) and (R)-2,2'-diethoxy-1,1'-binaphthyl-6,6'-dicarboxaldehyde **5a** (3.00 g, 7.53 mmol) dissolved in a mixture of dry DME (70 ml)/THF (20 ml) under an inert atmosphere at 0°C . The suspension was slowly allowed to reach r.t. and stirred for 21 h. The mixture was cautiously hydrolyzed with hydrochloric acid (500 ml) and shaken $3 \times$ with CH_2Cl_2 . The solvent of the combined organic phases was evaporated *in vacuo*. An oil was obtained, which was dissolved in CH_2Cl_2 (100 ml) and shaken with an acetic acid–sodium acetate buffer (1M, 200 ml) for 24 h. The organic phase was separated and the aqueous phase was shaken $3 \times$ with CH_2Cl_2 . The combined organic phases were washed $2 \times$ with KHCO_3 solution (10%) and water. After drying over MgSO_4 , the solvent was removed *in vacuo* after filtration. The solid obtained was purified by column chromatography on silica ($l = 11$ cm, $\varnothing = 4$ cm) using a mixture of ligroin (60–80)/AcOEt (1 : 1, v : v) as eluent. Recrystallization from CHCl_3 /ligroin (60–80) gave fine, slightly yellow needles which were dried in high vacuum. Yield 1.96 g (58%); m.p. 148°C . Anal: calcd. for $\text{C}_{30}\text{H}_{26}\text{O}_4$ (450.54) C 79.98, H 5.82; found C 80.02, H 5.85 per cent. $^1\text{H-NMR}$ (CDCl_3) δ (400 MHz): 9.72 (d, $-\text{CHO}, J = 8$ Hz, 2H), 8.02 (d, ArH^5 , 2H), 8.01 (d, $\text{ArH}, J = 9$ Hz, 2H), 7.60 (d, $-\text{CH}^-, J_{\text{trans}} = 15.9$ Hz, 2H), 7.46 (d, $\text{ArH}, J = 9$ Hz, 2H), 7.42 (dd, $\text{ArH}^7, J_{5,7} = 1.8$ Hz, $J_{7,8} = 9$ Hz, 2H), 7.13 (d, $\text{ArH}, J = 8$ Hz, 2H), 6.72 (dd, $-\text{CH}^-, J_{\text{trans}} = 15.9$ Hz, 2H), 4.10 (m, $-\text{OCH}_2-$, 4H), 1.09 (t, $J = 7$ Hz, $-\text{CH}_3$, 6H). $^{13}\text{C-NMR}$ (CDCl_3) δ (100.6 MHz): 193.51, 155.88, 152.87, 135.31, 130.97, 130.41, 129.17, 128.56, 127.63, 126.04, 123.84, 119.78, 115.73, 64.76, 14.75. IR (KBr): 1675 (s, C=O), 1616 (s, C=C), 972 (s, $-\text{C}-\text{H}_{\text{trans}}$) cm^{-1} . MS (FAB +): $m/z = 451$ (MH +). $[\alpha]_{\text{D}}^{25} = -734^\circ$ ($\text{CHCl}_3, c = 0.02$). UV-VIS (CHCl_3): λ_{max} (ϵ) = 261 (32600), 295 (53500), 343 (45200).

4.2.3. (R)-(E,E)-6,6'-Bis(4-bromostyryl)-2,2'-diethoxy-1,1'-binaphthyl **7a**

Diethyl (4-bromobenzyl)phosphonate (9.65 g, 31.42 mmol) and (R)-2,2'-diethoxy-1,1'-binaphthyl-6,6'-dicarboxaldehyde **5a** (5.0 g, 12.55 mmol) were dissolved in dry glyme (60 ml) under a nitrogen atmosphere. Sodium hydride (80% in mineral oil) (1.0 g, 33.3 mmol) was added at r.t. and the suspension was stirred magnetically for 3 days at r.t.. The mixture was cautiously hydrolyzed with water (300 ml) and the precipitate that formed was collected by filtration (glass frit) and washed thoroughly with water. The solid obtained was dried in air and dissolved in boiling CHCl_3 (c. 200 ml). Ether (c. 250 ml) was added to the cooled solution and the micro-

crystals that formed overnight in the freezer were filtered off, washed with ether, and dried in air. Yield 6.73 g (76%); m.p. 240–241°C. Anal: calcd. for $C_{40}H_{32}Br_2O_2$ (704.50) C 68.20, H 4.58, Br 22.68; found C 68.33, H 4.77, Br 21.56 per cent. 1H -NMR ($CDCl_3$) δ (400 MHz): 7.93 (d, ArH, $J = 9$ Hz, 2H), 7.87 (d, ArH⁵, $J_{5,7} = 1.7$ Hz, 2H), 7.35–7.48 (m, Ar, 12H), 7.22 (d, =CH⁻, $J_{trans} = 16.3$ Hz, 2H), 7.12 (d, ArH, $J = 9$ Hz, 2H), 7.03 (d, =CH⁻, $J_{trans} = 16.3$ Hz, 2H), 4.05 (m, -OCH₂-, 4H), 1.07 (t, -CH₃, 6H). ^{13}C -NMR ($CDCl_3$) δ (100.6 MHz): 154.61, 136.43, 133.77, 132.03, 131.63, 131.17, 130.41, 129.51, 129.24, 127.74, 126.86, 126.54, 125.86, 123.57, 120.45, 115.95, 65.04, 14.91. MS (FAB +): $m/z = 703$ (MH +), 705 (MH +), 707 (MH +). $[\alpha]_D^{25} = -397$ ($CHCl_3, c = 0.01$).

4.2.4. (*S*)-(E,E)-9,14-Bis(4-bromostyryl)dinaphtho[2,1-d:1',2'-f][1,3]dioxepin **7b**

Diethyl (4-bromobenzyl)phosphonate (7.63 g, 24.8 mmol) and (*S*)-dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-9,14-dicarboxaldehyde **5b** (4.0 g, 11.3 mmol) were dissolved in dry glyme (60 ml) under an inert atmosphere. Sodium hydride (80% in mineral oil) (1.0 g, 33.3 mmol) was added and the suspension was stirred magnetically for 28 h. The mixture was cautiously hydrolyzed with dilute HCl (400 ml) and the precipitate that formed was collected by filtration (glass frit) and washed thoroughly with water. After drying in air, a white powder was obtained, which proved to be pure by TLC. An analytical sample could be obtained by crystallization from CH_2Cl_2 /ether and subsequent drying at 100°C. Yield 7.45 g (100%); m.p. 252°C. Anal: calcd. for $C_{37}H_{24}Br_2O_2$ (660.41) C 67.29, H 3.66, Br 24.20; found C 67.47, H 3.67, Br 23.80 per cent. 1H -NMR ($CDCl_3$) δ (400 MHz): 8.09 (d, ArH, $J = 9$ Hz, 2H), 7.94 (d, ArH⁵, 2H), 7.55 (dd, ArH⁷, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H), 7.49 (d, Ar, 2H), 7.49 (m, Ar, 4H), 7.48 (d, Ar, 2H), 7.40 (m, Ar, 4H), 7.25 (d, =CH⁻, $J_{trans} = 16.3$ Hz, 2H), 7.12 (d, =CH⁻, $J_{trans} = 16.3$ Hz, 2H), 5.70 (s, -CH₂-, 2H). ^{13}C -NMR ($CDCl_3$) δ (100.6 MHz): 151.40, 136.11, 133.58, 131.95, 131.72, 131.66, 130.33, 128.94, 127.86, 127.77, 127.19, 127.14, 126.01, 123.52, 121.41, 121.33, 103.10. MS (FAB +): $m/z = 659$ (MH +), 661 (MH +), 663 (MH +). $[\alpha]_D^{25} = +1006$ ($CHCl_3, c = 0.02$).

4.2.5. (*R*)-(E,E)-4,4'-[2,2'-(2,2'-Diethoxy-1,1'-binaphthyl-6,6'-diyl)diethenyl]dibenzaldehyde **8a**

(*R*)-(E,E)-6,6'-Bis(4-bromostyryl)-2,2'-diethoxy-1,1'-binaphthyl **7a** (3.00 g, 4.26 mmol) was dissolved in dry THF (125 ml) under an argon atmosphere. The magnetically stirred solution was cooled to -78°C and a solution of *n*-BuLi in *n*-hexane (2.5 M) (7.0 ml, 17.5 mmol) was added at such a rate that the temperature did not exceed -70°C. After 6 h of stirring at this temperature, dry *N,N*-dimethylformamide (2.7 ml,

34.9 mmol) was added to the intensely coloured reaction mixture so that the temperature remained below -50°C. After stirring for 60 min at this temperature, the mixture was poured into HCl/ice (pH < 1) when a white solid precipitated. After standing overnight, the mixture was treated 4 × with CH_2Cl_2 , and the combined organic phases were washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure after filtration. The compound was submitted to column chromatography on silica-gel ($l = 15$ cm, $\varnothing = 6$ cm) using a CH_2Cl_2 /[(CH_2Cl_2 /AcOEt)(4 : 1, v : v)] gradient. After evaporation of the eluent under reduced pressure, a light yellow compound was obtained. Yield 1.79 g (70%); m.p. 213–215°C. Anal: calcd. for $C_{42}H_{34}O_4$ (602.73) C 83.70, H 5.69; found C 83.73, H 5.89 per cent. 1H -NMR ($CDCl_3$) δ (400 MHz): 9.98 (s, -CHO, 2H), 7.96 (d, ArH, $J = 9$ Hz, 2H), 7.93 (d, ArH⁵, 2H), 7.85 (d, Ar, $J = 8$ Hz, 4H), 7.65 (d, Ar, 4H), 7.48 (dd, ArH⁷, $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H), 7.43 (d, Ar, 2H), 7.39 (d, =CH⁻, $J_{trans} = 16.3$ Hz, 2H), 7.15 (d, ArH, 2H), 7.14 (d, =CH⁻, $J_{trans} = 16.3$ Hz, 2H), 4.07 (m, -OCH₂-, 4H), 1.09 (t, -CH₃, $J = 7$ Hz, 6H). ^{13}C -NMR ($CDCl_3$) δ (100.6 MHz): 191.41, 154.87, 143.58, 135.03, 134.06, 132.30, 131.64, 130.12, 129.48, 129.11, 127.68, 126.64, 126.44, 125.93, 123.57, 120.32, 115.92, 64.98, 14.88. IR (KBr): 1693 (s, C=O), 1597 (s, C=C), 967 (m, =C-H_{trans}) cm^{-1} . MS (FAB +): $m/z = 603$ (MH +). $[\alpha]_D^{25} = -672$ ($CHCl_3, c = 0.01$). UV-VIS ($CHCl_3$): λ_{max} (ϵ) = 309 (37000), 363 (57600).

4.2.6. (*S*)-(E,E)-4,4'-[2,2'-(Dinaphtho[2,1-d:1',2'-f][1,3]dioxepin-9,14-diyl)diethenyl]dibenzaldehyde **8b**

(*S*)-(E,E)-9,14-Bis(4-bromostyryl)dinaphtho[2,1-d:1',2'-f][1,3]dioxepin **7b** (2.16 g, 3.27 mmol) was dissolved in dry THF (100 ml) under an argon atmosphere. The magnetically stirred solution was cooled to -78°C and a solution of *n*-BuLi in *n*-hexane (2.5 M) (5.4 ml, 13.5 mmol) was added at such a rate that the temperature did not exceed -70°C. After 6 h of stirring at this temperature, dry *N,N*-dimethylformamide (3.1 ml, 40.0 mmol) was added to the intensely coloured reaction mixture so that the temperature remained below -50°C. After stirring for 70 min at this temperature the yellow mixture was poured into HCl/ice (pH < 1) with vigorous stirring. The mixture was allowed to reach r.t. and treated 3 × with CH_2Cl_2 . The combined organic phases were washed with aqueous NaCl, dried over $MgSO_4$ and the solvent removed under reduced pressure after filtration. The compound was submitted to column chromatography on silica-gel ($l = 10$ cm, $\varnothing = 4$ cm) using CH_2Cl_2 as eluent, giving small yellow needles after evaporation of the solvent. Yield 1.02 g (56%); m.p. 228–230°C. Anal: calcd. for $C_{39}H_{26}O_4$ (558.63) C

83.85, H 4.69; found C 83.79, H 4.76 per cent. $^1\text{H-NMR}$ (CDCl_3) δ (400 MHz): 10.01 (s, -CHO, 2H), 8.01 (d, ArH, $J = 9$ Hz, 2H), 8.01 (d, ArH 5 , 2H), 7.89 (br.d, Ar, $J = 8.4$ Hz, 4H), 7.69 (br.d, Ar, 4H), 7.60 (dd, ArH 7 , $J_{5,7} = 1.7$ Hz, $J_{7,8} = 9$ Hz, 2H), 7.52 (d, Ar, 2H), 7.51 (d, Ar, 2H), 7.43 (d, =CH $^-$, $J_{trans} = 16.3$ Hz, 2H), 7.24 (d, =CH $^-$, $J_{trans} = 16.3$ Hz, 2H), 5.73 (s, -CH $_2$ -, 2H). $^{13}\text{C-NMR}$ (CDCl_3) δ (100.6 MHz): 191.37, 151.68, 143.19, 135.31, 133.21, 131.93, 131.89, 131.68, 130.51, 130.15, 127.88, 127.68, 127.26, 126.79, 125.99, 123.52, 121.57, 103.13. MS (EI): $m/z = 558$ (M $^+$). IR (KBr): 1696 (s, C=O), 1599 (s, C=C), 963 (m, =C-H $_{trans}$) cm^{-1} . $[\alpha]_D^{25} = +1331^\circ$ (CHCl_3 , $c = 0.01$). UV-VIS (CHCl_3): $\lambda_{max}(\epsilon) = 247$ (49000), 346 (66700).

5. Conclusions

A number of chiral 6,6'-substituted binaphthol derivatives were synthesized for the first time by new or improved procedures. No mesophases were found in any of the compounds which indicates that the deviation from planarity of the BN-core is too large to allow the formation of mesophases. This is in accordance with the correlation between the decrease of the N-I transition temperature of the host solvent (which indicates the destabilization of the nematic host) and the molecular shape: open BN-diethers disturb the mesophase more than bridged BN-acetals. The new compounds possess functionalities and substituents which make them suitable for further synthetic transformations leading to potential BN-based liquid crystals.

The twisted structure makes it possible to use the new compounds as effective chiral dopants possessing unusually high twisting power β . The values of molar twisting power β_M of the bridged styryl derivatives **7b** and **8b** are among the highest reported. It was shown that the twisting power increases systematically with increasing length (shape) of the substituents in the 6,6'-positions, both for open and bridged compounds. This is in full accordance with the recently described shape model for the twisting power of chiral solutes in nematic LCs [44].

The twisting power of the closed BN-derivatives (type b, $n = 1$) was, depending on the temperature, on average between 3 and 5 times higher compared to the open BNs (type a, $n = 2$) in LC 1277 and LC 1630. The open chain derivatives show significant temperature dependence of twisting power; the magnitude of β_M usually decreased to about 60% of the initial value on heating from 20 to 65–70°C. The closed derivatives do not show this temperature dependence; their magnitude of β_M remains practically constant. This behaviour could be satisfactorily explained in terms of changes of population of *transoid* and *cisoid* states, which in turn are determined by the asymmetry of the potential energy function

describing the dependence of the molecular energy on the dihedral angle between the two naphthyl moieties.

The *cisoid*-conformation of all bridged BN-derivatives (type b, $n = 1$) and their absolute configuration was in full accordance with the determined helicities [11]. From the same measurements, the preferred conformations of all open chain BN-diethers (type a, $n = 2$) **3a–8a** were found to be *transoid* in LC 1277 and LC 1630, whereas compounds **1** and **2** prefer a *cisoid* conformation. In LC ZLI 1695 a *cisoid* conformation was found for **5a** and **8a**.

In summary, the molecular structures and conformations of BN-dopants could be directly correlated to their twisting power β , the temperature dependence of β , and the N-I transition temperatures of the LC mixtures. This leads to a further understanding of the nature of cholesteric induction by binaphthol derivatives in nematic liquid crystals.

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