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Conformational Analysis in Solution of C_2-Symmetric 1,1′-Binaphthyl Derivatives by Circular Dichroism Spectroscopy and Cholesteric Induction in Nematic Mesophases

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The twisting ability of a series of 1,1′-binaphthalene compounds used as dopants in nematic solvents has been related to the dihedral angle θ between the two naphthalene moieties. While in the case of the more flexible compounds the sign and value of the helical twisting power is affected by several structural features that prevent a simple assignment of the conformation, in the presence of a covalent bridge that restricts the rotation around the C(1)−C(1′) bond a reliable estimate of the conformational helicity could be obtained. This technique is complementary to CD spectroscopy that, for the investigated molecules, presents the same exciton patterns irrespective of the actual θ value.

Introduction

1,1′-Binaphthyl derivatives have been largely employed in enantioselective catalysis[1] and in other chiral molecular recognition processes.[2]

One of the most important structural variable of these compounds is the dihedral angle θ between the two naphthyl planes, which is defined by C(8a)−C(1)−C(1′)−C(8a′). The largely unrestricted rotation around the C(1)−C(1′) bond ($\theta = 60−120°$)[3] in the unbridged derivatives makes it possible to accommodate 2,2′-substituents irrespective of their size and, eventually, to chelate a large variety of metal centers without appreciable strain. Furthermore, 1,1′-binaphthyl compounds of a given configuration can have conformations of opposite helicity depending on θ (Figure 1). For $0° < \theta < 90°$ (s-cis conformation) an (*R*)-1,1-binaphthyl shows a *P* helicity, while for $90° < \theta < 180°$ (s-trans conformation) it shows an *M* helicity.[4]

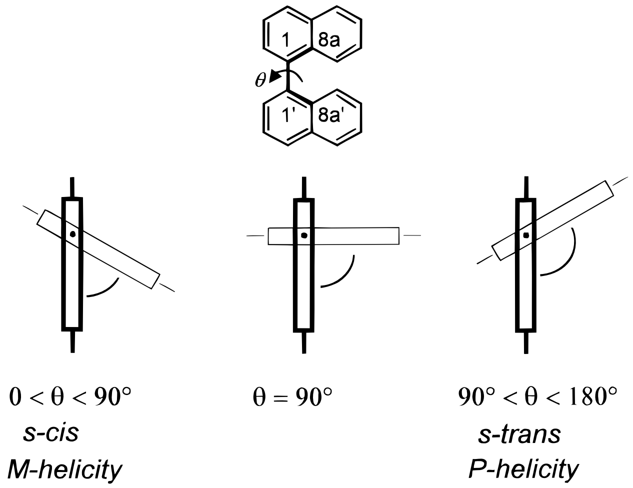

Figure 1. Numbering and conformers of 1,1′-binaphthalene.

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(4) In this context, *P* and *M* helicity refers to the (conformational) helicity along the biaryl axis irrespectively of the sequence rule of the substituent eventually present, as defined in Figure 1: see, for example: Testa, B. In *Principles of Organic Stereochemistry*; Dekker: New York, 1979; p 71.

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The importance of controlling θ in chiral discrimination processes has recently been addressed.[5,6a] These studies on the conformation of binaphthyl derivatives rely on the use of molecular mechanics or semiempirical structure calculations[5,6a] or on data from X-ray crystal structure analyses.[7]

The experimental estimation of the θ value of 1,1′-binaphthalene compounds in solution is somewhat hampered by the C_2 symmetry of the compounds that prevents the use of the most common NMR experiments for conformational investigation.[8] Chiroptical techniques may afford, in this situation, qualitative or semiquantitative information on the dihedral angle.[9−12] The exciton model[9] of the optical activity was first used by Mason and co-workers[10] to derive the relation between the amplitude of a CD spectrum and the dihedral angle θ. More recently, Salvadori and co-workers[13] derived an analogous relation between another spectral parameter, the exciton splitting, and the dihedral angle θ. However, these approaches are not of general validity and lead to reliable information only in the absence of auxochromic groups and when conjugation between the naphthyl subunits can be excluded.[13]

CD spectroscopy exploits the analysis of the CD couplet originating from the long-axis polarized ^1B_b electronic transition of the naphthalene chromophore at approximately 230 nm.[9] For the *R*-configuration, an s-cis conformation ($0° < \theta < 90°$) shows a bisignate signal with a negative branch at low energy and a positive one at high energy (negative couplet). On increasing θ first a critical value is obtained for which the couplet vanishes, then the couplet inverts its sign. The critical value has been estimated to be around 100−110° for unsubstituted 1,1′-binaphthalene,[10] but it is greatly affected by the presence of substituents on the naphthyl rings.

A completely different approach to obtain information on the dihedral angle θ of C_2-symmetric 1,1′-binaphthalenes is based on the phenomenon of the cholesteric induction:[14] the addition of a nonracemic chiral compound to a nematic liquid crystal induces a cholesteric phase characterized by pitch and handedness (*P* or *M*). The different ability of a chiral dopant to twist the nematic phase is expressed by the twisting power $\beta = (p \cdot x_d \cdot \mathrm{ee})^{-1}$, where p is the pitch, x_d the dopant mole fraction, and ee its enantiomeric excess; the sign of β is taken positive for a right-handed (*P*) cholesteric and negative for a left-handed (*M*) one.

For stereochemical purposes, β characterizes a chiral substance as well as the classical optical rotatory power [α] does. However, the cholesteric induction technique is a nonspectroscopic method based on solute−solvent interactions and can therefore be expected to be sensitive mainly to the effective molecular shape of a compound and less to the electronic characteristics of the substituents present.[15] It has been extensively applied to conformational and configurational analysis[16−23] and to solve various stereochemical problems.[14] When both the solute and the nematic solvent have a biaryl structure, it is possible to correlate the helicity of the biaryl solute to the handedness of the induced cholesteric phase: therefore, if the absolute configuration is known, the s-cis or s-trans conformation can be deduced from the sign of the twisting power β. For 1,1′-binaphthalenes with an absolute configuration of (a*R*), a negative β-value indicates a s-cis conformation and a positive β-value a s-trans one.

In the present paper, we report a conformational study of a class of 1,1′-binaphthalene-2,2′-diol derivatives by means of the combination of chiroptical (CD) and liquid crystal techniques.

Results and Discussion

Induced Cholesteric Phases: Twisting Power Measurements. The (*aR*)-1,1′-binaphthalene-2,2′-diol derivatives investigated in the present work are listed in Chart 1. They can be grouped into three classes, **A**−**C**: class **A** comprises open-chain compounds, class **B** 2,2′-bridged compounds, and class **C** bis(1,1′-binaphthalene) derivatives. The corresponding helical twisting powers β measured in the two nematic solvents E7 and MBBA are reported in Table 1, while, for comparison, a few data on related derivatives (**D** and **E**) taken from the literature are reported in Table 2.

Class A Compounds. Nonbridged, conformationally flexible compounds **A**[2h] show relatively small twisting powers β (up to 25 μm^{-1}) whose signs depend not only on the nature of the substituents X and Y but also on

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(6) (a) Lustenberger, P.; Martinborough, E.; Mordasini Denti, T.; Diederich, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 747. (b) Lustenberger, P.; Welti, R.; Diederich, F. *Helv. Chim. Acta* **1998**, *81*, 2190.

(7) The case of 1,1′-binaphthalene is remarkable to point out the role of the crystal packing in the determination of the actual conformation: in the enantiomerically pure form 1,1′-binaphthalene crystallizes in a s-trans conformation (θ = 103.1°) (Kuroda, R.; Mason, S. F. *J. Chem. Soc., Perkin Trans. 2* **1981**, 167) while in the racemic composition as an s-cis rotamer (θ = 68.6°) (Kerr, K. A.; Robertson, J. M. *Chem. Soc. B* **1969**, 1146). See also: Kress, R. B.; Duesler, E. N.; Etter, M. C.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1980**, *102*, 7709.

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(14) A review of the applications of this technique in solving stereochemical problems is given in: Spada, G. P.; Proni, G. *Enantiomer* **1998**, *3*, 301.

(15) An attempt to relate the two quantities for chiral biaryls has been discussed in: Gottarelli, G.; Osipov, M. A.; Spada, G. P. *J. Phys. Chem.* **1991**, *95*, 3879.

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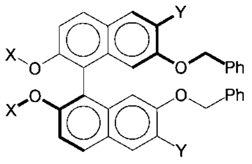
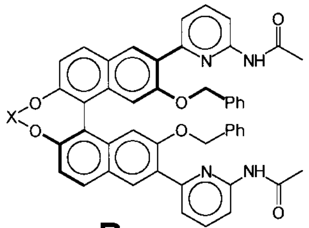
Chart 1



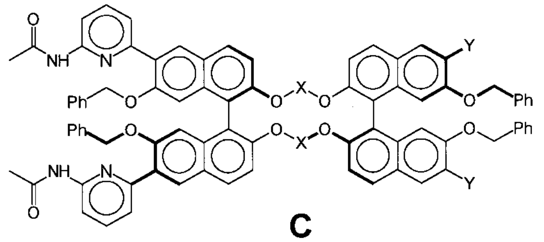
1 X = H Y = Br
2 X = CH_2OCH_3 Y = Br
3 X = H Y = 6-acetamido-2-pyridyl
4 X = CH_2OCH_3 Y = 6-acetamido-2-pyridyl
5 X = $C_{12}H_{25}$ Y = 6-acetamido-2-pyridyl
6 X = $CH_2CH(C_2H_5)_2$ Y = 6-acetamido-2-pyridyl
7 X = $SiMe_2Bu^t$ Y = 6-acetamido-2-pyridyl

A



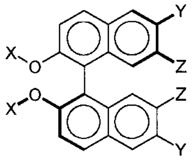
8 X = CH_2
9 X = $CH_2CH_2N^+(CH_3)_2CH_2CH_2$, I^-
10 X = CH_2CH_2N $(COOC_2H_5)CH_2CH_2$
11 X = CH_2CH_2N (CH_3) CH_2CH_2
12 X = $CH_2C{\equiv}CCH_2$
13 X = $CH_2(m\text{-}C_6H_4)CH_2$

B



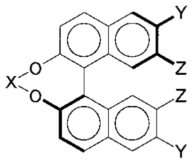
C

14 X = CH_2CCCH_2 Y = 6-acetamido-2-pyridyl
15 X = $CH_2(p\text{-}C_6H_4)CH_2$ Y = 6-acetamido-2-pyridyl
16 X = $CH_2(p\text{-}C_6H_4)CH_2$ Y = Br



17 X = H Y = H Z = H
18 X = H Y = H Z = Br
19 X = H Y = H Z = BzlO
20 X = H Y = Br Z = H
21 X = CH_3 Y = H Z = H
22 X = CH_3 Y = H Z = Br
23 X = Et Y = H Z = H
24 X = Et Y = Br Z = H
25 X = Bn Y = H Z = H
26 X = $C_{12}H_{25}$ Y = H Z = H

D



27 X = CH_2 Y = H Z = H
28 X = CH_2 Y = H Z = Br
29 X = CH_2 Y = H Z = BzO
30 X = CH_2 Y = Br Z = H
31 X = $(CH_2)_3$ Y = H Z = H
32 X = $(CH_2)_4$ Y = H Z = H

E

Figure 2. The s-trans conformation of (*aR*)-**13**.[6a] The substituents in the 6,6′ and 7,7′ positions were removed for clarity.

the nematic solvents. This behavior has been already described in the literature[21] and is likely to be a consequence of flat-bottomed potential energy curve (as a function of θ)[13,19] leading to the *quasi*-orthogonal conformation ($\theta \sim 90°$) that is expected to have a negligible β.[24] The different LC's can, in this case, exert a different stabilization on the s-cis and s-trans conformations[19] modifying the actual conformation and/or the solute alignment. For example, compound **5** shows twisting powers of almost the same small absolute value but opposite sign in the two solvents investigated. As already pointed out, when the solvent has a biaryl structure (such as E7) it may act as a probe of the binaphthyl helicity and the sign of the twisting power is indicative of a s-cis or s-trans conformation; this approach has been successfully applied[16−21] to many 1,1′-binaphthalene-2,2′-diol derivatives, and therefore, we will limit our analysis to this solvent.

With the exception of **3** and **6** all the **A**-derivatives show in E7 positive β's that could be associated with a *P*-helicity of the binaphthyl unit and hence, for the (*aR*)-configuration, to a s-trans conformation. This seems to support the idea that 2,2′-disubstitution of the 1,1′-binaphthalene compound with groups unable to form intramolecular H-bonds and the 7,7′-disubstitution tend to force the conformation toward the s-trans conformation. Only compound **3**, in fact, shows a well-defined negative value of β, which is in agreement with literature data (see Table 2, compounds **D**).

Class B Compounds. In the presence of a covalent bridge connecting the C(2) and C(2′) atoms, the freedom to rotation about the C(1)−C(1′) axis is restricted, and therefore, compounds **B**[6a] are more rigid than unbridged compounds of the **A**-type. The bridged compounds **E** reported in the literature, possess much higher twisting powers (50−80 μm^{-1}) than the corresponding open derivatives **D** and **A** (0−30 μm^{-1}). These high values of β are accounted for on the basis of a rigid structure characterized featuring a dihedral angle θ around 55°.[18] In fact the correlation between the twisting powers of 1,1′-binaphthyl compounds and the aryl-aryl dihedral angle was confirmed by theoretical calculations:[24] the maximum absolute value of β is predicted for $\theta = 45$ or 135°, while β is zero at θ around 90°. While the negative twisting powers of **27**−**32** reflect the *M*-helicity of the biaryl group present in these s-cis bridged (*aR*)-compounds, an experimental check that rigid s-trans derivatives exhibit positive β values was still lacking.

Systematic structural variation of the covalent bridge X allowed to obtain 1,1′-binaphthalene compounds with dihedral angles θ ranging from ca. 60 to 96° as determined by computational molecular modeling[6a] using the OPLS* force field (see Table 1, compounds B): derivatives **9**−**11** adopt a s-cis conformation [*M*-helicity for (*aR*)-configuration] while compounds **12** and **13** a s-trans one [*P*-helicity for (*aR*)-configuration] (see Figure 2). It is remarkable to point out that, despite the presence of relevant goups in the 6 and 7 positions, the handedness of the cholesteric phase matches the helicity *P*/*M* of the binaphthyl unit: increasing θ, the twisting power β spans from relatively high negative values for **8** and **10** to relatively high positive value for **12** and **13** passing through the negligible value of **11**. The crossover is observed at a value of θ not far from the theoretical value of 90° calculated for the unsubstituted bynaphthyl.[24]

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Table 1. Twisting Powers β of (a*R*)-Configured 1,1′-Binaphthalene Derivatives 1−16 in the Nematic Solvents MBBA[a] and E7[b] and the CD Features, λ and $\Delta\epsilon$, of the ^1B_b Transition of the Naphthalene Chromophore

		θ ($\Delta\theta$)[c]/deg		β (SD)/μm^{-1} in MBBA	β (SD)/μm^{-1} in E7	λ/nm ($\Delta\epsilon$/M^{-1} cm^{-1})
1	**A**			−25.7 (0.1)	+8.1 (0.1)	236 (+313), 257 (−314)
2	**A**			+1.8 (0.5)	+13.7 (0.6)	240 (+351), 254 (−446)
3	**A**			−26.6 (1.0)	−8.6 (0.4)	248 (+182), 270 (−190)
4	**A**			−13.5 (0.2)	+10.5 (1.0)	250 (+224), 269 (−228)
5	**A**	80 (10)	*M*/(*P*)	−21.5 (0.1)	+24.8 (0.4)	250 (+204), 272 (−201)
6	**A**	90 (10)	*M*/*P*	−12.0 (0.2)	−1.9 (0.3)	
7	**A**	90 (10)	*M*/*P*	nd	+6.2 (0.1)	
8	**B**	60 (5)	*M*	−20.8 (1.9)	−33.6 (0.3)	245 (+211). 270 (−231)
9	**B**	72 (7)	*M*	nd	nd	248 (+164), 272 (−202)
10	**B**	78 (5)	*M*	−39.0 (1.3)	−65.6 (1.4)	246 (+155), 275 (−187)
11	**B**	86 (4)	*M*	−5.1 (0.6)	−2.5 (0.2)	246 (+150), 271 (−190)
12	**B**	91 (5)	*P*	+17.1 (4.1)	+40.0 (15)	250 (+264), 267 (−260)
13	**B**	96 (3)	*P*	+22.6 (0.3)	+95.2 (1.9)	256 (+304), 273 (−213)
14	**C**			+28.2 (5.1)	+94.4 (1.6)	249 (+386), 268 (−417)
15	**C**			nd	−102.9 (7.4)	252 (+382), 273 (−389)
16	**C**			−239.5 (2.3)	−242.3 (9.9)	244 (+413), 258 (−216), 271 (−225)

[a] MBBA: *N*-(4-methoxybenzilidene)-4-butylaniline (from Aldrich). [b] E7: eutectic mixture (from Merck) of 4-cyano-4′-pentyl/-heptyl/-octyloxybiphenyl and 4-cyano-4′-(4″-pentylphenyl)biphenyl]. [c] θ and $\Delta\theta$ are taken from ref 6a. $\Delta\theta$ provides an estimate for the conformational flexibility around the chirality axis.

Table 2. Twisting Powers β of (*R*)-derivatives 17−32 in Biphenyl-Type LC's Reported Previously in the Literature

		β/μm^{-1}	LC	lit.
17	**D**	−32	K15	17
18	**D**	+26.1	E7	21
19	**D**	−5	E7	21
20	**D**	−15.5	LC 1277	19
21	**D**	−1.5	K15	17
22	**D**	+6.8	E7	21
23	**D**	+10	LC 1277	19
24	**D**	+19	LC 1277	19
25	**D**	−1.4	K15	17
26	**D**	+22	E7	12
27	**E**	−85	K15	16
28	**E**	−68	E7	21
29	**E**	−80	E7	21
30	**E**	−57	LC 1277	19
31	**E**	−80	K15	16
32	**E**	−79	K15	16

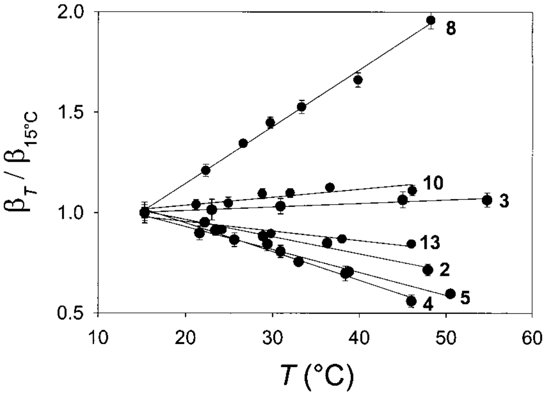

Figure 3. Normalized twisting powers as a function of temperature in E7.

Temperature Dependence. The temperature dependence of the helix pitch of an induced cholesteric phase is quite complex and so far not completely understood. In the case of biaryls it has been interpreted in terms of conformational equilibrium between two or more local energetic minima.[25] In this view, the restricted rotation around the C(1)−C(1′) bond in the bridged derivatives should lead to β values practically unaffected by temperature changes as experimentally observed for some derivatives.[19,23] The behavior of β with increasing temperature for a few derivatives of class **A** and **B** is shown in Figure 3. In contrast to our expectations, the trend described above was not observed here. In fact, the β-value is practically constant for the open-chain derivative **3**, while the more pronounced pitch variation is observed for the bridged compound **8**; in this latter compound the temperature effect is even higher than in the corresponding open-chain compound **4**. This finding seems to suggest that the temperature dependence may not be attributed only to conformational mobility around the C(1)−C(1′) axis, but rather to all conformational changes of the molecules, e.g., rotation about the binaphthalene−pyridine axis. Furthermore, the temperature-dependent alignment of the solute with respect to the nematic solvent molecules is of fundamental importance in the chiral induction.[26] Analogous difficulties in interpreting the temperature behavior were faced in doped lyotropic nematics and have been discussed in ref 27.

Class C Compounds. Compounds **C**[6b] show very high twisting power apparently not related in a simple manner to the helicity (*P* or *M*) of the two binaphthalene moieties. In fact, β is not an additive property and compounds **C** cannot simply be considered the "sum" of two **A** or **B**-type molecules. The building up of a molecule with two stereogenic axes by joining two (although homochiral) derivatives with one sterogenic element generates a completely new molecule with its own specific shape chirality. As a matter of fact, the solute−solvent interaction will be different (and peculiar): e.g., the anisometry of the dimeric molecules **C** is quite different from that of the simplest compounds of the type **A** and **B**. This affects the alignment and hence the chirality transfer.

Induced Cholesteric Phases: DSC Measurements. In an attempt to obtain more information on the solute−solvent interactions, we measured the clearing point of the cholesteric solutions. It is known, in fact, that the addition of a nonmesogenic compound to a liquid crystal

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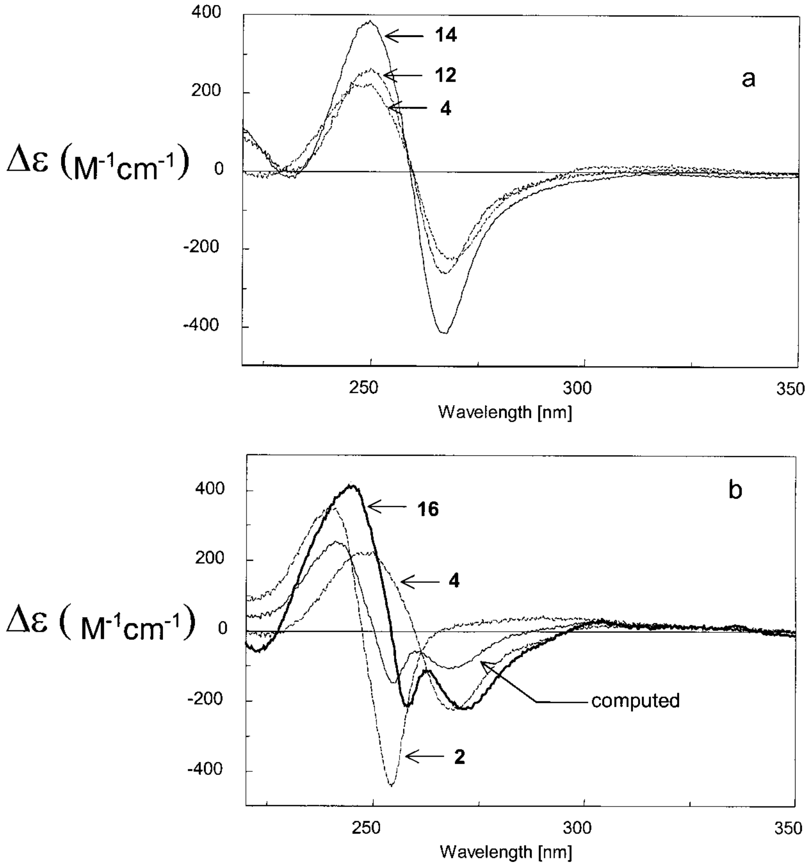

Figure 4. Frame a: CD spectra of derivatives **4**, **12**, and **14** as selected examples of **A**, **B**, and **C** compounds. Frame b: CD spectra of derivatives **16**, **2**, and **4** and the computed spectrum obtained averaging spectra of **2** and **4**.

Table 3. Experimental δ_I Values in the Nematic Host E7 (Obtained via Linear Regression Analysis by Plotting T_{NI} vs x_d)

		δ_I/K	r^2
1	**A**	−608	0.988
2	**A**	−744	0.993
8	**B**	−464	0.67
10	**B**	−1160	0.991
12	**B**	−88	0.70

may induce an increase or a decrease of the clearing temperature T_{NI} in comparison to the clearing temperature of the pure liquid crystal $T_{NI}°$.[28] At low dopant mole fraction, T_{NI} varies linearly with concentration according to $T_{NI} = T_{NI}° + \delta_I x_d$. The proportionality constant δ_I constitutes a measure of the propensity of the dopant to stabilize or destabilize the liquid crystal phase. In aromatic compounds, δ_I is influenced by electrostatic as well as dispersion forces.[29] We measured by differential scanning calorimetry the T_{NI} at three different x_d for some of the **A**-type and **B**-type derivatives and the results obtained are reported in Table 3. Schaumburg and coworkers[19] related the high destabilization of the liquid crystal matrix caused by the high-dihedral angle open-chain binaphthyls ($\theta \approx 90°$) to their low twisting powers and the small destabilization caused by the bridged binaphthalenes featuring small dihedral angles ($\theta \approx 50°$) to their high twisting powers (even if exceptions were described). Our results, however, seem to exclude a direct relation between rigidity (bridged vs unbridged) or θ and the propensity to stabilize the phase. The ability to transfer their own molecular chirality to the solvent bulk cannot be described only in terms of intermolecular forces.[24,26]

CD Measurements. As pointed out in the Introduction, CD spectroscopy may give useful information about the conformation of biaryl derivatives. The CD spectra of three selected compounds (**4**, **12**, and **14**, as examples of class **A**, **B**, and **C** derivatives, respectively) are reported in Figure 4a, and the CD features in the spectral range 230−300 nm of the investigated compounds are reported in Table 1. From an inspection of these data it appears that all the compounds show an intense negative couplet in correspondence of the allowed, long-axis polarized ^1B_b transition of the naphthol chromophore at ca. 230 nm. In the frame of Mason's approach,[10] this spectral feature is indicative (for the *aR* configuration) of θ smaller than the "critical" value for which the couplet vanishes estimated to be around 110°. An attempt to correlate the amplitude[10] or the exciton splitting[13] with θ did not succeed, and therefore, CD spectroscopy is unable to discriminate the cis/trans conformations with respect to the C(1)−C(1′) bond.

Remarkably, the CD spectrum of the nonsymmetric dimeric compound **16** (Figure 4b) shows that the couplets of the two binaphthyl units are *quasi*-additive which is in contrast to what was observed for the helical twisting power β. In fact, the summing up of the CD spectra of derivatives **2** and **4** (with almost the same chromophores present in **16**) is very similar to the actual spectrum of **16**. This is expected for compounds in which the two

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exciton systems are not-interacting and the sole responsible of the CD signals in the UV/Vis region.

Conclusions

Circular dichroism and the induction of cholesteric mesophases constitute two complementary and powerful methods to single out subtle conformational details such as the variation of the dihedral angle θ between the two naphthalene moieties of a series of 1,1′-binaphthalene compounds.

While in the case of the more flexible compounds **A** the sign and value of the helical twisting power is affected by several structural features that prevent a simple conformation assignment, in the presence of a covalent bridge (in compounds **B**) that restricts the rotation around the C(1)−C(1′) bond, a reliable estimate of the conformational helicity could be done. Systematic structural variation of the covalent bridge allowed to obtain 1,1′-binaphthalene compounds with dihedral angles θ ranging from ca. 60 to 96° and the handedness of the cholesteric phase matches the helicity *P*/*M* of the binaphthyl unit. These results support the model for which the chiral transfer from binaphthyl dopants to the biaryl solvent bulk is mediated by the chiral shape of the solute.

Experimental Section

Synthesis and purification of compounds **1**−**7** (class A), **8**−**13** (class B), and **14**−**16** (class C) are reported in refs 2h, 6a, and 6b, respectively. DSC experiments were performed with a Perkin-Elmer DSC7 instrument. Cholesteric pitch values and helical handedness were obtained with the lens version of the Grandjean-Cano method[30,31] using a Standard 16 Zeiss microscope equipped with a Linkam thermostating system.

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