It is clearly worth remarking, in connection with the earlier discussion of Marcus theory, that the correlation shown in Figure 1 indicates a complete insensitivity of the reaction rates to either bond energies, given by $\Delta\Delta G°_{BDE}$, or to reaction free energies, given by $\Delta G°_{ion}$, which, as shown in Table III, span a considerable range for the various nucleophiles.

**Acknowledgment.** This work was supported by Grant CHE 8205767 from the National Science Foundation. I am grateful to Prof. H. King and to Prof. J. McIver for enlightening discussions of molecular orbital theories, Koopmans' theorem, and other esoteria.

**Registry No.** $OH^-$, 14280-30-9; $CN^-$, 57-12-5; $N_3^-$, 14343-69-2; $HOO^-$, 14691-59-9; $CH_3O^-$, 3315-60-4; $CF_3CH_2O^-$, 24265-37-0; $C_6H_5O^-$, 3229-70-7; *n*-$PrNH_2$, 107-10-8; $H_2O$, 7732-18-5; *n*-$PrS^-$, 20733-14-6; $C_6H_5S^-$, 13133-62-5; $OCl^-$, 14380-61-1; $CH_3CO_2^-$, 71-50-1; $NO_2^-$, 14797-65-0; $F^-$, 16984-48-8; piperidine, 110-89-4; pyronine, 92-32-0.

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# Induction of the Cholesteric Mesophase in Nematic Liquid Crystals: Mechanism and Application to the Determination of Bridged Biaryl Configurations

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**Abstract:** It is shown that the helicity of optically active bridged biaryl molecules is the main factor determining their high twisting power in biphenyl nematic liquid crystals. A mechanism of induction of the cholesteric phase was deduced from the orientation of the solute molecules, determined by linear dichroism and from the solvent effect. These results show that it is also possible to correlate the absolute configurations of optically active bridged biaryl compounds to the sign of their twisting power in biphenyl nematics.

When a chiral "guest molecule" is dissolved in a nematic liquid crystal, its molecular chirality is transferred to the solvent which becomes organized in a macrostructural helical cholesteric structure.[2-4]

A cholesteric structure is characterized by its handedness and pitch. Equal amounts of enantiomeric "guests" of equal enantiomeric purity induce helical structures with identical pitch and opposite handedness.[3] Different substances show a different ability to twist a nematic phase. The twisting power of a chiral dopant can be defined as[5,6]

$$\beta_M \approx (pcr)^{-1}$$

where $p$ is the pitch ($\mu m^{-1}$), $c$ is the concentration (moles of solute/moles of solution), and $r$ is the enantiomeric purity of the dopant.

The twisting power $\beta_M$ and its sign [(+) for a P helix and (−) for an M helix of the induced cholesteric] characterize the chiral solute in a way similar to the specific optical rotation [$\alpha$]. However, the physical origin of the two quantities is entirely different. The origin of the optical rotation depends on interactions between light and molecules, while the twisting power originates from interactions between molecules of solute and solvent.[6-8] Quantity $\beta_M$, a molecular property dependent on the liquid crystalline matrix, can give information on the chiral dopant. On the one hand, the passage from molecular to macrostructural chirality somehow amplifies the molecular asymmetry, and this can be used to detect traces of optically active substances,[9] to follow racemization kinetics on extremely small scale experiments,[10] and also to characterize molecules with very low optical rotations such as compounds chiral by isotopic substitution.[11] On the other hand, the variations of $\beta_M$ with the molecular structure of the inducing chiral compound and, for a given dopant, with the liquid crystal used as solvent can give information concerning the mechanism of induction and also allow the formulation of an interaction model between solute and solvent, able to predict the handedness of the induced cholesteric mesophase.

In a previous work[4] on optically active *trans*-stilbene oxide and related molecules, we proposed a model of induction in which the chirality is transferred from the chiral inducer to the nearest neighbor molecule of the solvent through chiral conformations; the latter serves as a template for the near neighbor and so on, thus justifying the observed high values of $\beta_M$.

In this paper we report our results on the chiral biphenyl system. Optically active twisted biaryls should display strong interactions with liquid crystals of the biaryl type because of their structural analogy, and therefore a study of their twisting powers should also give evidence to confirm or disregard our hypothesis on the mechanism of induction. We specifically restricted our study to only bridged derivatives where the helicity of the biaryl system is unambiguous in order to apply our model to the correlation of configurations.

## Results and Discussion

Pitch values were determined by means of the Grandjean–Cano method which is based on the observation of the discontinuity lines appearing when a cholesteric liquid crystal is inserted into a cell

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**Table I.** Twisting Powers of Optically Active Biaryl Compounds in Biphenyl-Type Liquid Crystals

| biaryl | dopant biaryl helicity | $\beta_M{}^a$ in $E_7{}^b$ | $\beta_M{}^a$ in PCB$^c$ |
|---|---|---|---|
| (+)-1 | $P^{28a}$ | +69 | |
| (−)-2 | $M^{37}$ | −65 | |
| (−)-3 | $M^{28b}$ | −71 | |
| (−)-4 | $M^{39}$ | | −55 |
| (−)-5 | $M^{28d}$ | −21 | |
| (+)-6 | $P^{40}$ | | +85 |
| (+)-7 | $P^{40}$ | | +80 |
| (+)-8 | $P^{40}$ | | +79 |
| (+)-9 | $P^{42}$ | +8 | |
| (+)-10 | $P^{38}$ | +24 | |
| (−)-11 | $P^{19,43}$ | +54 | |
| (−)-12 | $P^{19}$ | +64 | |
| (−)-13 | $M^{21}$ | −5 | |

$^a$ Values corrected to 100% ee. A positive value for $\beta_M$ corresponds to a right-handed cholesteric (P helix). $^b$ $E_7$: a mixture of 4-cyano-4′-*n*-aryl- and 4′-*n*-alkylbiphenyl from Merck. $^c$ PCB: 4-cyano4′-*n*-pentylbiphenyl.

**Table II.** Twisting Powers of Optically Active Binaphthyl Compounds 7 and 8 in Nematic Liquid Crystals (LC)

| nematic LC$^a$ | $\beta_M$ 7 | $\beta_M$ 8 |
|---|---|---|
| PCB | +80 | +79 |
| MBBA | +56 | +65 |
| phase 1052 | +38 | +42 |
| ZLI | +35 | |

$^a$ MBBA = *p*-methoxybenzylidene-*p*-*n*-butylaniline. Phase 1052 from Merck = a mixture of aromatic esters. ZLI 1167 from Merck = a mixture of bicyclohexane derivatives.

of variable thickness[7,12,13] and/or with the "droplet" method.[6,14,15] Both methods gave identical values within experimental error.

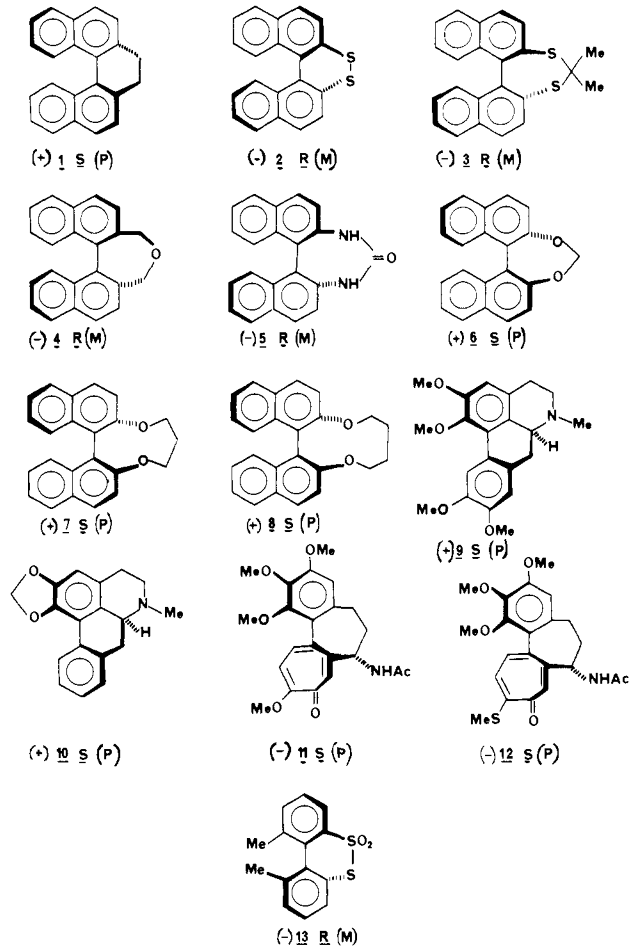
The handedness of the helices was determined by means of the elegant method recently described by Heppke and Oestreicher.[16] A cholesteric solution is placed between a glass plate with planar alignment (parallel rubbing) and a lens with concentric surface alignment (circular rubbing). With those boundary conditions, a P cholesteric originates a left-handed double spiral and an M cholesteric a right-handed one.

The sign of the rotatory power of the cholesteric mesophase[17,18] always confirmed the assignments based on the double spiral method.

In Table I the characteristics of the cholesteric structures induced in biphenyl-type liquid crystals by a series of synthetic and natural bridged biaryl systems (Scheme I) are reported.

It is certainly gratifying to notice that, despite the important differences in the chemical structures, molecules **1**–**13** having the biaryl system twisted with a P helicity or an M helicity show positive or negative twisting power, respectively. In other words, the main factor determining the chirality of the induced mesophase is the twist sense of the biaryl moiety.

Scheme I



Quantitative values of $\beta_M$ are generally very high and considerably larger than those observed for *trans*-stilbene oxide and analogous molecules[4] which were already much larger than those of chiral alcohols[7] and other variously substituted derivatives.[23] These high values were, as anticipated before, somehow expected as bridged biaryl derivatives are conformationally rigid, and being structurally very similar[4,6,8] these derivatives should interact very well with the biphenyl-type liquid crystals.

The variations of $\beta_M$ for compounds **7** and **8** in different liquid crystals, reported in Table II, are in agreement with these observations; the maximum value is in fact observed in the biphenyl-type liquid crystal.

## The Orientation of the Biaryl System Inside the Mesomorphic Solvent and a Possible Model of Induction.

Any structural interpretation of the induction of cholesteric mesophases must be based on the knowledge of the orientation of the inducing molecules with respect to the local director.

The linear dichroism (LD) of guest molecules oriented by nematic solvents transparent in the UV–visible region can afford two types of information: if the main orientation of the guest molecule is known, data concerning the polarization of the electronic transitions become available and vice versa if the polarizations of the transitions are known, the orientation of the molecule is obtained.

When no mixed polarisations are present, a very simple relationship links the LD $|E_{\|}(\lambda) - E_{\perp}(\lambda)|$ to the "average absorption"[24] $|(E_{\|}(\lambda + E_{\perp}(\lambda)|$ and to the Saupe order parameter $S_{uu}$ of the $u = x, y, z$ molecular axes (eq 1), where $E_{\|}(\lambda)$ and $E_{\perp}(\lambda)$ are the

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(19) X-ray analysis of Colcemid[20a] (*N*-desacetyl-*N*-methylcolchicine) shows that the tropolonoid ring is planar and makes a dihedral angle of 54° with the benzene ring. The twist of the two rings is P. Similar results were obtained for 7-oxodesacetamidocolchicine and 7-oxodesacetamidoisocolchicine.[20b]

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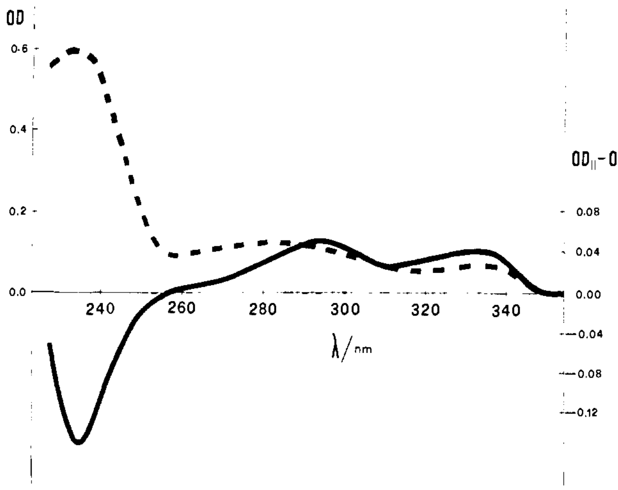


**Figure 1.** The absorption (- - -) and linear dichroism (—) of racemic **8** dissolved in the nematic phase ZLI 1167 (mixture of bicyclohexyl derivatives).

Scheme II

optical densities of the two perpendicularly plane polarized components of the incident radiation.

$$\frac{E_{\parallel} - E_{\perp}(\lambda)}{E_{\parallel}(\lambda) + E_{\perp}(\lambda)} = \frac{3S_{uu}}{2 + S_{uu}} \qquad (1)$$

The LD spectrum of racemic **8** dissolved in the nematic mixture of bicyclohexyl derivatives ZLI 1167 is shown in Figure 1.

The nature of the electronic transitions of naphthalene is well understood.[25] In particular the weak low-energy transition observed at ca. 310 nm is long-axis polarized ($^1L_b$) and is followed, at higher energy, by a medium-intensity short-axis-polarized $^1L_a$ transition and at ca. 220 nm by a strong long-axis-polarized $^1B_b$ transition. The effect of a 2-methoxy substituent on the absorption spectrum is strong only on the low-energy $^1L_b$ transition whose intensity is considerably enhanced, while the other transitions are not modified.[26]

The polarizations of the $^1B_b$ and $^1L_a$ transitions should therefore not be strongly affected by the methoxy substituent while that of the $^1L_b$ should be shifted toward the short-axis direction according to Platt's diagram (Scheme II).[27]

The absorption spectrum of binaphthyl **8** is very similar to that of the "parent" 2-methoxynaphthalene with a slight shift of all bands toward lower energy. The most relevant interaction between the two chromophores is probably the exciton interactions of the $^1B_b$ transitions, which, in optically active derivatives, is responsible for the bisignate CD in the 200–250-nm region.[28a,b] The allowed component of the exciton couplet is polarized along the twofold symmetry axis of the molecule.

In the spectrum in Figure 1, a negative LD is associated with this band indicating that the twofold symmetry axis is perpendicular to the nematic director. The positive LD at ca. 280 nm corresponds to the $^1L_a$ transition. Therefore the short axis of the naphthalene chromophore must be parallel to the nematic director. The LD at ca. 310 nm is again positive in agreement with the fact that most of the intensity comes from the $OCH_2$ substituent, as discussed above.

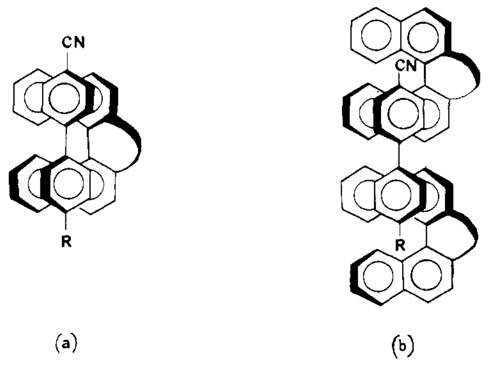
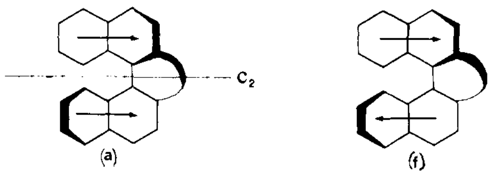


**Figure 2.**

Scheme III. Allowed (a) and Forbidden (f) Coupling of the "Long-Axis"-Polarized $^1B_b$ Transition of the Naphthalene Chromophore in a Bridged Binaphthyl System



Binaphthyl **8** is therefore oriented with the axis joining the two naphthyl groups parallel to the nematic director, i.e., the long axis of the bicyclohexyl molecules of the solvent. A similar orientation of the solute molecules was observed also in the case of spirobifluorene in the same nematic solvent.[29]

There are no substantial reasons[30] to predict a different orientation in the biphenyl-type liquid crystal. On the contrary the interactions of the aromatic groups of the solute with the benzene rings of the solvent should be stronger than in the case of the aliphatic solvent. Accordingly, the $\beta_M$ values of optically active **8** are higher in the biphenyl LC than in the bicyclohexyl one (see Table II).

The conformation of 4,4′-substituted biphenyls in nematic liquid crystalline solution show nonplanar conformations with torsion angles from ca. 30° to ca. 80° according to the substituents.[31,32] Therefore it is reasonable to assume that such nonplanar conformations exist also in biphenyl-type liquid crystals such as PCB or $E_7$. Obviously in the nematic phase, couples of mirror-image conformations are equally probable but interconvert rapidly.

The chiral biaryl inducer, aligned with its biaryl axis parallel to the biphenyl axis of the solvent, can have close contact and interact only with molecules having the same chirality (the same chiral conformation) (Figure 2a). At the very low experimental concentrations of the inducer leading to very high values of $\beta_M$, it seems unrealistic to postulate for statistical reasons a model in which one molecule of LC interacts with two molecules of inducer (Figure 2b). The chirality is therefore transferred from the inducer to a near molecule of solvent and from this to the next near and so on via chiral conformations until the chiraly ordered aggregate attains a metastable size and thermally disintegrates as it aggregates further.

This mechanism is similar to that proposed for *trans*-stilbene oxide in MBBA[4] but more efficient as the chiral conformation of the bridged binaphtyls is well fixed. Although *trans*-stilbene oxide shows structural similarities with the liquid crystal used as solvent (MBBA), the handedness of the twist is the result of a preferred conformation of the doping molecule. One chiral

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conformer must certainly be preferred and interact better with the solvent but others are also likely to be present, and consequently a lower twisting power is observed. The situation is very similar in the case of unbridged chiral biphenyls. We observed indeed lower $\beta_M$ values,[33] a result consistent with the possibility of two conformations of opposite helicity, each one inducing an opposite twist sense.

## Conclusion

The helicity of optically active bridged biaryl molecules is likely to be the main factor determining their very high twisting power in biphenyl nematic liquid crystals. The chirality of the dopant is transferred to the nematic through chiral conformations: a biaryl doping molecule having a P helicity leads to a cholesteric mesophase of the same P helicity.

It is therefore possible to correlate the absolute configurations of optically active bridged biaryl compounds to the sign of their twisting power in biphenyl nematics. For such molecules this method could be considered as a complementary tool to the well-documented chiroptical techniques[39] generally used for the assignment of the absolute configurations of chiral biaryls when strongly perturbing substituents are present.[28b] This is particularly evident in the case of natural compounds containing the twisted biphenyl system substituted by hydroxy and methoxy groups.[34a] The recent paper by Snatzke et al.[34b] on the CD spectra of colchicine and analogous alkaloids emphasizes the problem in the interpretations of CD curves arising from variations of the chromophores. In the present study colchicine and thiocolchicine are correlated to the other biaryl systems with no apparent difficulties.

## Experimental Section

Compounds **1**, **2**, **3**, **5**, and **13** were kindly supplied by Prof. S. F. Mason.[28b–d] The characteristics of compound **1** are identical with those described.[36] Characteristics of molecules **2** and **3** are identical with those reported.[37]

Although the optical purities of derivatives **1**, **2**, and **3** are not exactly known, they were assumed to be 100%, based on the fact that both enantiomers of their precursor carboxylic acids[36] and sulfonic acids[37] were obtained with optical rotations practically equal and opposite; from both enantiomers of the precursors, both enantiomers of **1**, **2**, and **3**, having equal and opposite optical rotations, were obtained.

The optical purity of **13** is not known.

Alkaloids glaucine (**9**) and colchicine (**11**) were commercial products purchased from K–K Chemicals. Alkaloid (+)-aporheine (**10**) was kindly supplied by Prof. J. Slavik[38] and thiocolchicine (**12**) was kindly provided by Prof. B. Danieli.

Samples **4** (28% ee[39]) and **6** (70% ee) were kindly supplied by Dr. Welvart.

Finally, compounds **7** and **8** were prepared from the corresponding optically active binaphthol (enantiomeric purity 70%). Microscopic measurements were carried out following the method described in ref 7 using a Zeiss polarizing microscope and Galileo plano-convex lenses of radius 20–40 mm. The concentric alignments were obtained by pressing the lens on a tissue paper attached to a rotating plate. In order to obtain the spirals more easily, both the lens and the glass plate were treated with [(*N*-methylamino)propyl)]triethoxysilane or with polyvinyl alcohol.

The LD spectra were recorded by a modulated technique (JASCO LD attachment to the J-500A spectropolarimeter) using a bicyclohexyl nematic liquid crystalline matrix transparent to the UV radiation (E. Merck; ZLI 1167) and a surface coupling agent in order to get linearly anisotropic samples. The calibration and the experimental details of the technique are discussed in rêf 24.

**Acknowledgment.** We are indebted to NATO for the partial support of this research (Grant No. RG 081-81). G.G. and B.S. thank the Italian CNR and the Ministero P.I. G.S., M.H., and R.Z. thank CNRS (ERA 687) for financial support. We are grateful to Prof. S. F. Mason for stimulating discussions and for providing derivatives **1**, **2**, **3**, and **5**, and **13**, to Prof. J. Slavik for a sample of (+)-aporheine, to Prof. B. Danieli for a sample of thiocolchicine, and to Drs. Welvart, Cabaret, and Mazaleyrat for compounds **4** and **6**. Finally we thank société Hoffmann-La-Roche (Basel) for providing us large quantities of PCB.

**Registry No.** (+)-**1**, 848-42-0; (−)-**2**, 79252-43-0; (−)-**3**, 87728-92-5; (−)-**4**, 67179-63-9; (−)-**5**, 87728-93-6; (+)-**6**, 86289-51-2; (+)-**7**, 87728-94-7; (+)-**8**, 87728-95-8; (+)-**9**, 475-81-0; (+)-**10**, 2030-53-7; (−)-**11**, 64-86-8; (−)-**12**, 2730-71-4; (−)-**13**, 87728-96-9; E$_7$, 63748-28-7; PCB, 40817-08-1; phase 1052, 69772-69-6; ZLI 1167, 67009-49-8; MBBA, 26227-73-6.

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