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Conformational and Configurational Analysis of 4,4′-Biphenanthryl Derivatives and Related Helicenes by Circular Dichroism Spectroscopy and Cholesteric Induction in Nematic Mesophases

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Coupling the analysis of circular dichroism (CD) spectra with the study of cholesteric mesophases induced in nematic liquid crystals (LC) allows one to deduce some stereochemical features of 3,3′-disubstituted-4,4′-biphenanthryl derivatives. The exciton coupling model can explain the CD spectra of the open-chain derivatives, thus confirming their absolute configuration; the LC technique indicates an *s-trans* conformation in agreement with molecular mechanics computations. Compounds with a bridge between the 3 and 3′ positions are conformationally rigid and similar in shape, and their absolute configuration can be predicted by the LC technique. On the other hand, their CD spectra are different and not easy to interpret as a consequence of the different chromophores present.

Introduction

Chiral biaryl systems are present in several compounds ranging from natural products[1] (*e.g.* ellegitanines,[2] ancistrobrevines,[3] and the complex systems of michelleamines[4]) to synthetic derivatives; the latter have been largely employed[5] as chiral auxiliaries in stereoselective reactions.

The 1,1′-binaphthalene backbone has been extensively used as the parent core in chiral auxiliaries, and most of these derivatives have a C_2 symmetry because of the presence of two identical substituents at the 2,2′-positions. These substituents very often contain heteroatom donors which are either directly bound to the aryl nucleus or are separated by a single carbon atom.[5] The well-known BINAP is a paradigm of the efficiency of such derivatives in asymmetric synthesis.[6]

Owing to the relevance of such structures in organic chemistry, spectroscopic studies aimed at determining their configuration and conformation have received considerable attention in the past years.

The problem to be faced in the stereochemical analysis of biaryl systems is the following: biaryl derivatives, such as 1,1′-binaphthyls, of a given configuration, *e.g.* *R*, can have conformations of opposite helicity depending on the dihedral angle θ between the planes containing the two aromatic moieties. For $0° < \theta < 90°$ (*s-cis* conformation) the helicity is *M*, while for $90° < \theta < 180°$ (*s-trans* conformation) the helicity is *P* (see Figure 1).

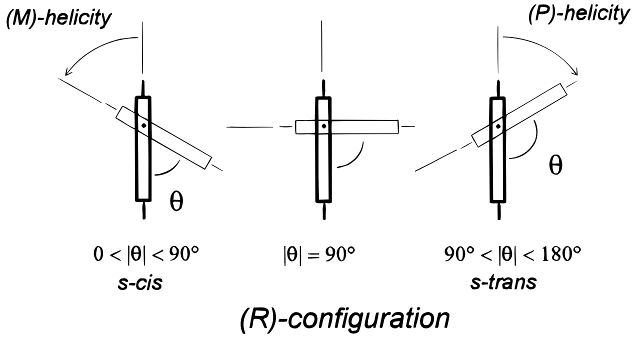

Figure 1.

Analysis of the CD spectra has been largely employed in order to have information about the conformation of biaryl derivatives;[7] later, a technique based on the induction of cholesteric phases in nematic liquid crystals was introduced.[8]

The analysis of the Cotton effect arising from the exciton coupling[7] of the intense electronic transition located in the two aryl moieties can give information about the dihedral angle θ. In the case of 1,1-binaphthyl derivatives of *R* configuration, the exciton pattern due

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

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Table 1. Spectroscopic Characteristics of (*R*)-1-5 and (*M*)-6 in Cyclohexane

	absorption, λ (log ϵ)	circular dichroism, λ ($\Delta\epsilon$)
(*R*)-**1**	366 (3.41), 348 (3.46), 315 (4.36), 302 (4.36), 261 (4.74), 244 (4.67)	367 (+3.8), 342 (−10.3), 329 (−9.5), 305 (+2.0), 273 (−143), 256 (+142), 244 (+100, sh), 219 (−23)
(*R*)-**2**	371 (3.38), 353 (3.41), 324 (4.47), 310 (4.48), 265 (4.79), 247 (4.78)	372 (+9.3), 355 (+8.3), 331 (+31.5), 276 (−196), 250 (+186), 217 (−11.2)
(*R*)-**3**	312 (3.70), 300 (3.78), 259 (4.16)	316 (+8.9), 284 (−11.9), 257 (+23.8), 224 (−9.1)
(*R*)-**4**	356 (3.04), 339 (3.09), 302 (4.36, sh), 252 (4.88)	355 (+2.4), 339 (+2.2), 376 (+33), 287 (−24), 266 (−49), 247 (+123), 224 (−73)
(*R*)-**5**	263 (4.36)	400 (−3.0), 343 (−48), 321 (−41), 287 (−19), 261 (+158), 222 (−101)
(*M*)-**6**	398 (3.84), 382 (3.87), 320 (4.41), 305 (4.41), 261 (4.79), 241 (4.72)	408 (+3.3), 380 (−3.3), 326 (−40), 310 (−17), 252 (−73), 240 (+60)

to the coupling of the ^1B_b long-axis polarized transition is negative for a *s-cis* conformation, but inverts its sign from negative to positive when θ passes through a critical value of *ca.* 100−110°.[9]

The LC technique is based on the cholesteric induction phenomenon: the addition of a chiral compound to a nematic liquid crystal induces a cholesteric mesophase,[8] characterized by pitch and handedness (*P* or *M*). The ability of a solute to twist the nematic phase is expressed by the twisting power $\beta = 1/(pcr)$, where p is the pitch, c the molar fraction of the solute, and r its enantiomeric excess.

The phenomenon of cholesteric induction can be applied to solve different stereochemical problems ranging from configurational[10] and conformational[11] analysis to racemization studies,[12] to the detection of small quantities of chiral compounds or compounds of low optical activity.[13]

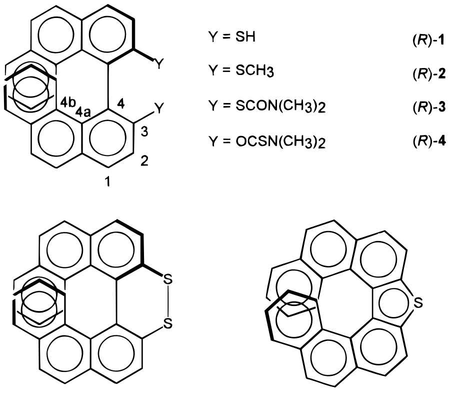
When both the chiral solute and the nematic solvent have a biaryl structure, the helicity of the chiral biaryl unit may be related to the cholesteric handedness: a (*P*)-biaryl induces a (*P*)-cholesteric (positive β), while a (*M*)-biaryl induces a (*M*)-cholesteric (negative β).[8]

The aim of this study is to extend the study to other biaryl compounds, the 4,4′-biphenanthryl derivatives, and to related helicenes in order to define the configuration and conformation of these chiral solutes, and also to obtain a better understanding of the solute−solvent interactions at the basis of the cholesteric induction.

Results and Discussion

The open-chain 4,4′-biphenanthryl derivatives (−)-(*R*)-**1**, (+)-(*R*)-**2**, (+)-(*R*)-**3**, and (+)-(*R*)-**4** and the bridged compound (−)-(*R*)-**5** were obtained[14] through a stereoconservative procedure starting from (−)-(*R*)-4,4′-biphenanthrene-3,3′-diol, whose absolute configuration was established unambiguously[15,16] by chemical correlation and X-ray diffraction of the corresponding dimethyl ether.

Chart 1



(*R*)-**5** (*M*)-**6**

Compound (−)-(*M*)-**6** with very low optical purity was obtained[14] during the thermal rearrangement of (+)-(*R*)-**4**. Evidence has been provided that racemization does not precede, but instead follows thiophene formation. Samples of (−)-(*M*)-**6** with higher ee were obtained[14] by resolution with (−)-(*R*)-TAPA,[17,18] thus confirming the absolute *M* configuration of the eptaetherohelicene (−)-**6**.

Circular Dichroism. The CD spectral features of the compounds investigated, (*R*)-**1**−5 and (*M*)-**6**, are reported in Table 1.

Open-Chain Biphenanthryl 1. The CD and absorption spectra of the parent compound (−)-(*R*)-**1** is reported in Figure 2. The absorption spectrum is dominated by the presence of bands associated with the transitions of the phenanthrene chromophore: the L_b transition at *ca.* 350 nm, the L_a transition at *ca.* 300 nm, and the B_b transition at *ca.* 260 nm.[19] The CD spectrum is dominated by the intense negative conservative exciton couplet associated with the B_b transition at *ca.* 260 nm, while small dichroic signals are present in correspondence to the first two transitions.

These spectral features are quite similar to those reported[16] for its oxygenated analogue (−)-(*R*)-4,4′-bi-

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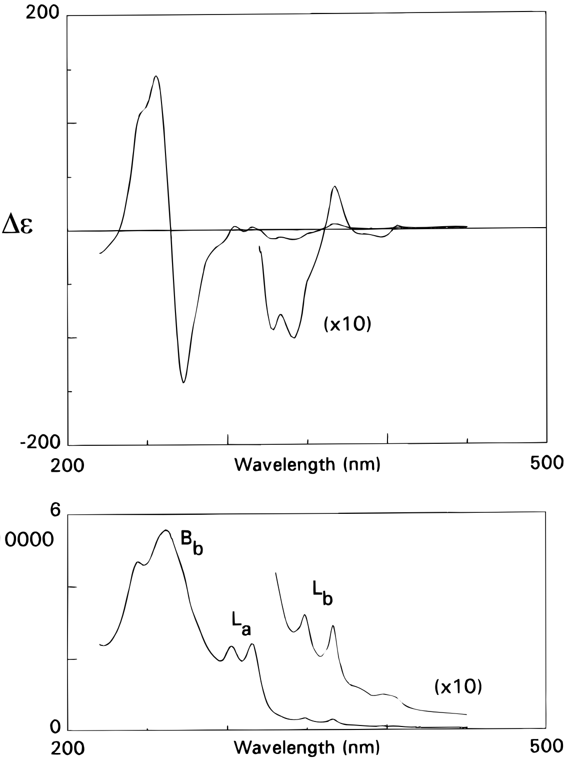

Figure 2. Circular dichroism (upper part) and absorption (lower part) spectra of (−)-(*R*)-**1** in cyclohexane.

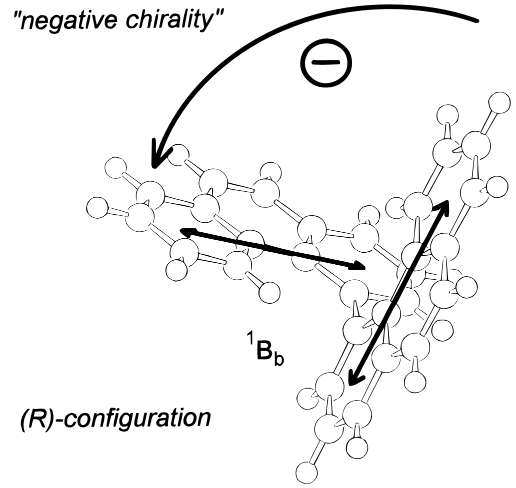

Figure 3. Negative chirality of the ^1B_b long-axis polarized transition for the (*R*)-4,4′-biphenanthryl backbone.

phenanthrene-3,3′-diol, thus indicating that the substitution of the oxygen with sulfur does not greatly affect the chromophore.

The CD spectrum can be interpreted in terms of the exciton coupling theory.[7,9] The B_b transition of the phenanthrene[19] chromophore (main peak at 254 nm, ϵ 65500) is long-axis polarized.[20] Following a qualitative exciton approach, a negative couplet around 260 nm indicates a negative skewness (chirality) of the transition moments located in the phenanthryl moieties (Figure 3); this was expected for a compound with *R* absolute configuration and a dihedral angle of *ca.* 105° (from molecular mechanics computations[21]). From a qualitative estimation, using point dipoles located on the 4a−4b bond (see *infra*), the chromophoric chirality seems to be insensitive to the rotation around the 4−4′ bond.

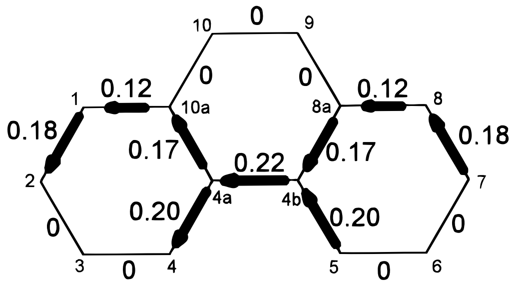

Figure 4. The vectorial bond orders in the ^1B_b transition of phenanthrene as a result of CNDO/S-CI computations (see text).

In order to support the above conclusions, calculations of the CD spectrum of the unsubstituted compound (*R*)-4,4′-biphenanthrene were carried out, using the all-order coupled oscillator model proposed by De Voe.[22] As previously discussed in detail,[23] a De Voe calculation of CD (*i.e.* $\Delta\epsilon$ as a frequency-dependent function) is based, similarly to the classical exciton model, on the subdivision of the molecule into a set of interacting subsystems, the chromophores. In the present case, (*R*)-4,4′-biphenanthrene is built up by two phenantherene chromophores; the geometrical parameters are given in terms of the most stable molecular conformation provided by molecular mechanics calculations on (−)-(*R*)-**1**. As reported above, the ^1B_b transition of the phenanthrene chromophore was represented by a single oscillator oriented along the long-axis of the chromophore; in order to reproduce quantitatively the absorption spectrum of **1**, a dipolar strength of 60 D^2 was used. In an initial calculation, the coupled transition dipole moments were located in the center of the middle ring. Assuming arbitrarily the *R* absolute configuration for **1**, a positive couplet was obtained, in disagreement with the experimentally observed negative couplet. As pointed out by Mason,[24] in most cases the particular location of the excitation moment is not critical for the exciton analysis of the CD spectrum. However, in the case of (+)-2,7-diaminotriptycene and (−)-1,5-diamino-9,10-dihydro-9,10-ethenoantracene, this is not true and the correct location of the transition dipole moments is given only by calculating it with the dipole velocity procedure.[24] With this observation in mind, a CNDO/S-CI calculation was carried out with standard parameters, using a phenantherene geometry obtained by molecular mechanics calculations. Within this scheme, the ^1B_b transition can be correctly represented by a single excitation from the MO 32 to the MO 35 (considering that the coefficient of this configuration in the CI expansion is larger than 0.9). By using the c_i coefficient of the carbon p-orbitals, the vectorial bond order ($c_{\mu,32}c_{\nu,35}$-$c_{\mu,35}c_{\nu,32}$) of the ^1B_b transition, representing the transitional charge momentum along the carbon atoms μ and ν, was obtained, following Mason's procedure. These values are reported in Figure 4: they clearly show that the center of gravity of the ^1B_b transition is not in the middle of the central

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[20] Thulstrup, E. W.; Michl, J.; Eggers, J. H. *J. Phys. Chem.* **1970**, *74*, 3868. Thulstrup, E. W. *J. Mol. Struct.* **1978**, *47*, 359.

[21] MMX, Serena Software, P. O. Box 3076, Bloomington, IN 47402.

[22] De Voe, H. *J. Chem. Phys.* **1964**, *43*, 3199.

[23] For a discussion of the application of this model to the solution of structural problems, see: Rosini, C.; Zandomeneghi, M.; Salvadori, P. *Tetrahedron: Asymmetry* **1993**, *4*, 545.

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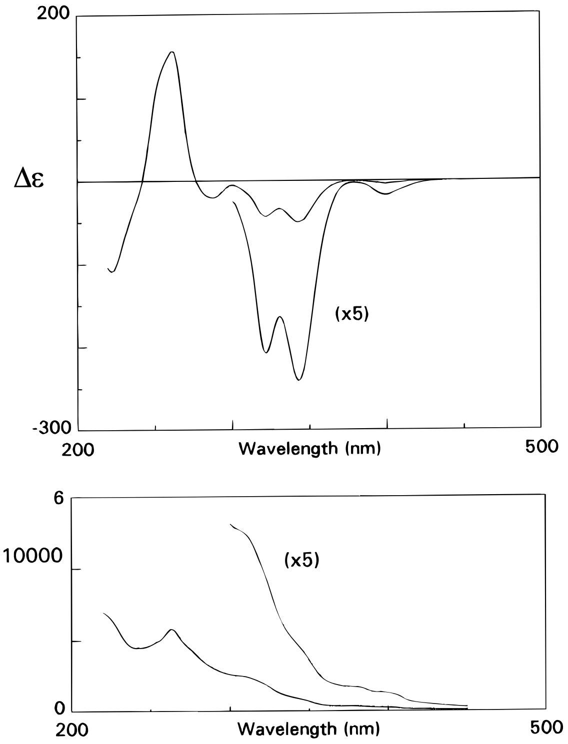


Figure 5. Circular dichroism (upper part) and absorption (lower part) spectra of (−)-(*R*)-**5** in cyclohexane.

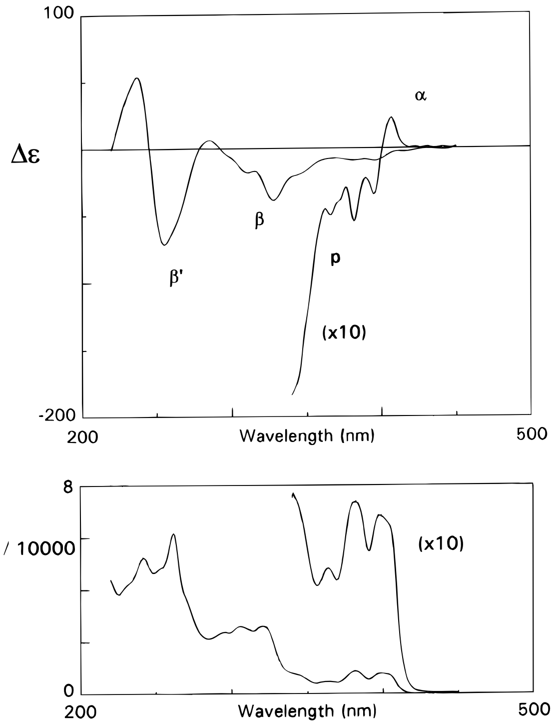
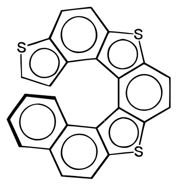


Figure 6. Circular dichroism (upper part) and absorption (lower part) spectra of (−)-(*M*)-**6** in cyclohexane.

Chart 2



(*M*)-**7**

ring, but is shifted toward the center of the 4a−4b bond. It is also interesting to note that bonds 8a−9, 9−10, 10−10a do not contribute to the overall transition dipole moment. The De Voe calculation was then repeated changing the location of the interacting dipoles (*i.e.* in the middle of the 4a−4b bond): a negative couplet (λ 262 nm, $\Delta\epsilon$ −107; λ 246 nm, $\Delta\epsilon$ +108) was obtained in very good agreement with the experimental data.

Open-Chain Biphenanthryls 2−4. Also the dimethyl sulfide (+)-(*R*)-**2** and the corresponding oxygen analogue[16] show CD spectra dominated by a negative conservative exciton coupling at *ca.* 260 nm, very similar to that described for (−)-(*R*)-**1**.

When the spectroscopic influence of the substituents in the 3,3′ positions becomes important, *e.g.* for compounds (+)-(*R*)-**3** and (+)-(*R*)-**4**, the couplet corresponding to the B_b transition is no longer conservative, and the negative bands (for the derivative **4** there is a fine structure with two resolved negative bands) become less intense (see Table 1).

Bridged Biphenanthryl 5. The CD and absorption spectra of the bridged compound (−)-(*R*)-**5** are reported in Figure 5. The CD spectrum does not exhibit an exciton pattern around 260 nm, but only a positive, single-signed band. This behavior is similar to that reported for an analogous compound, the formyl ketal of (−)-(*R*)-4,4′-biphenanthrene-3,3′-diol.[16] Due to the presence of a disulfide bridge between the phenanthryl moieties, the dihedral angle is relatively small (*ca.* 52° from molecular mechanics computations[21]); this constraint suggests that the two chromophoric units cannot be treated as independent (a basic assumption of the exciton treatment).

Biphenanthrothiophene 6. The CD and absorption spectra of the bridged compound (−)-(*M*)-**6** are reported in Figure 6. Starting from low energy, a small positive dichroic signal (α-band), a small negative one (p-band), a relatively intense negative signal (β-band), and finally an intense negative band (β'-band), followed by a positive one, are observed. This spectrum resembles those exhibited by a series of (−)-(*M*)-heterohelicene consisting of fused benzene and thiophene rings, described by Groen and Wynberg.[25] In particular, the similarity of the CD spectra of (−)-(*M*)-**6** and the heteroeptahelicene (−)-(*M*)-**7**, in which three thiophene units are present, is striking. This supports the finding that these compounds have the same *M* configuration.[26]

Cholesteric Induction. The twisting powers of the biphenanthryl derivatives (*R*)-**1**−6, together with those relative to two helicene compounds (*M*)-**8**, **9**,[29] are reported in Table 2.

Biphenanthryls 1−5. From the examination of Table 2, it is possible to observe that the bridged derivative (*R*)-**5** has negative β while the open-chain derivatives (*R*)-

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[25] Groen, M. B.; Wynberg, H. *J. Am. Chem. Soc.* **1971**, *93*, 2968.

[26] The absolute configuration of a (+)-(*P*)-etero[6]helicene containing a benzodithiophene unit was assigned by X-ray diffraction[27] and chemical correlation.[28] Also π-SCF calculations of the optical activity support this assignment.[25,27] The analogy of CD spectra[25] of heterohelicenes containing thiophene moieties in different positions and the behavior of the latter when treated with TAPA resolving agent[17] allows one to extend the configurational assignment to different helicenes.

[27] Groen, M. B.; Stulen, G.; Visser, G. J.; Wynberg, H. *J. Am. Chem. Soc.* **1970**, *92*, 7218.

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[29] The absolute configuration of hexahelicene **8** was determined by X-ray diffraction,[30] chemical correlation,[28,31] and SCF calculation.[32] The configuration of helicene **9** was deduced by SCF calculation.[33]

Table 2. Twisting Powers of Compounds (*R*)-1−5, (*M*)-6, (*M*)-8 and (*M*)−9 in Nematic Solvent E7[a]

compounds	β (μm^{-1})	cholesteric handedness
(*R*)-**1**	+8	P
(*R*)-**2**	+28	P
(*R*)-**3**	+7.5	P
(*R*)-**4**	+16	P
(*R*)-**5**	−13	M
(*M*)-**6**	−20	M
(*M*)-**8**	−55	M
(*M*)-**9**	−9	M

[a] See note to Table 3.

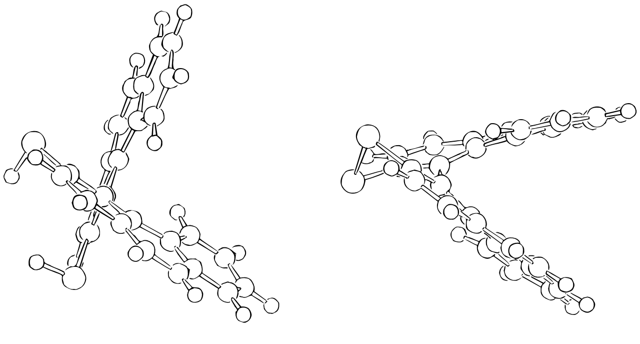
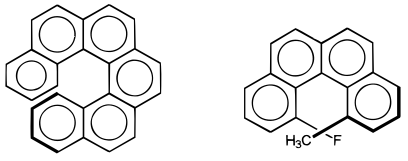

(*R*)-**1** (*R*)-**5**

Figure 7. The most stable conformation (MMX routine) of compounds (*R*)-**1** and (*R*)-**5**.

Chart 3



(*M*)-**8** (*M*)-**9**

1−**4** have positive β. As discussed above, the sign of β reflects the helicity of the aromatic moieties (at a fixed configuration).

All the investigated compounds have the same *R* configuration, hence the negative value observed for **5** indicates *M* helicity in agreement with the *s-cis* conformation around the 4−4′ bond imposed by the disulfide bridge (see Figure 7). This behavior is in agreement with previous observations on bridged binaphthyl derivatives.[8]

On the other hand, in the case of open chain derivatives, the biaryl conformation is not predictable *a priori* on the basis of the molecular structure. Molecular mechanics computations[21] seem to indicate that the most stable conformation for the parent compound **1** is *s-trans* with a dihedral angle not far from 105°. The analysis of the induced cholesteric can give further information about the conformation: positive β values exhibited by compounds (*R*)-**1**−**4** indicate *P* helicity of the biaryl unit and therefore *s-trans* conformation.

Helicenes 6, 8, 9. As the origin of the cholesteric induction is the interaction between a solute molecule and the nematic solvent, in contrast to CD spectra, the β values are more sensitive to the molecular shape and less to the electronic characteristic of the chromophoric groups present.[8,10,11] The molecular shape of (*M*)-helicenes resembles that of the (*R*)-biphenanthryl derivative **5** (see Figure 7); accordingly, all the helicenes investigated have negative twisting powers. This reflects the same shape-chirality, even if the two groups of molecules (helicenes and biphenanthryls) have different chromophores.

Model of Cholesteric Induction. A few years ago, a mechanism was proposed for the transmission of chirality from the dopant to the nematic solvent:[10] the chiral guest selects chiral conformations of the solvent molecules lying next to it, and these in turn induce chiral conformations in the nearest neighbor molecules of the solvent and so on.

This mechanism seems operative in the case of binaphthyl derivatives as inducers: the orientation of the solute is with the axis joining the two naphthyl groups parallel to the nematic director. This approach was used to understand the cholesteric induction caused by heptalenes,[34] propellerlike molecules in which two different helicities can be detected depending on the relative solute−solvent orientation.

In order to apply the original model, one needs to assume a close contact between solute and solvent along a specific direction. In the present compounds, the overall shapes of the molecules are likely to be globular: they are not very anisometric, hence it is difficult to assume a preferential alignment.

A modification of the model proposed for binaphthyls and discussed above could apply to all the compounds investigated which have either biphenanthryl or helicene structure. In the original model, the two aromatic moieties are chirally twisted, but essentially planar (this is true for biphenyl or binaphthyl compounds). In the case of biphenanthryls with $\theta \neq 90°$ (and also in the case of helicenes, of course), the molecular shape resembles that of an overall-twisted structure. Taking as an example 4,4′-biphenanthrene, we can see from molecular mechanics calculations[21] that, if the dihedral angle 3−4−4′−3′ is *ca.* 90°, the two aryl moieties are planar or quasiplanar. On the contrary (still for the *R* configuration), if this angle is 120°, the steric hindrance between the terminal benzene ring and the C3 positions imposes a deviation from planarity, and the *P* helicity along the 4−4′ bond is transferred to each phenanthrene unit that consequently becomes twisted (see Figure 8). The opposite *M* helicity is induced in the phenanthryls when the dihedral angle is 60° (*M* helicity along the 4−4′ bond).

In this model, the helicene molecules represent a limiting case in which the helicity is continuous along the whole molecule. With reference to hexahelicene (see Figure 9), several skewed biaryl units can be recognized (AC, BD, CE, and DF along the directions *a*, *b*, *c*, and *d*): all these biphenyl units have the same *M* helicity. The crystal structure of some helicene derivatives clearly shows this distortion.[14,35]

It seems that the chirality sensed by the biphenyl-type nematic solvent is the skewness between two alternate (noncontiguous) benzene or thiophene rings. Taking as an example the (*M*)-helicene **6** (Figure 10), one can recognize *M* helicity between benzene rings C and E.

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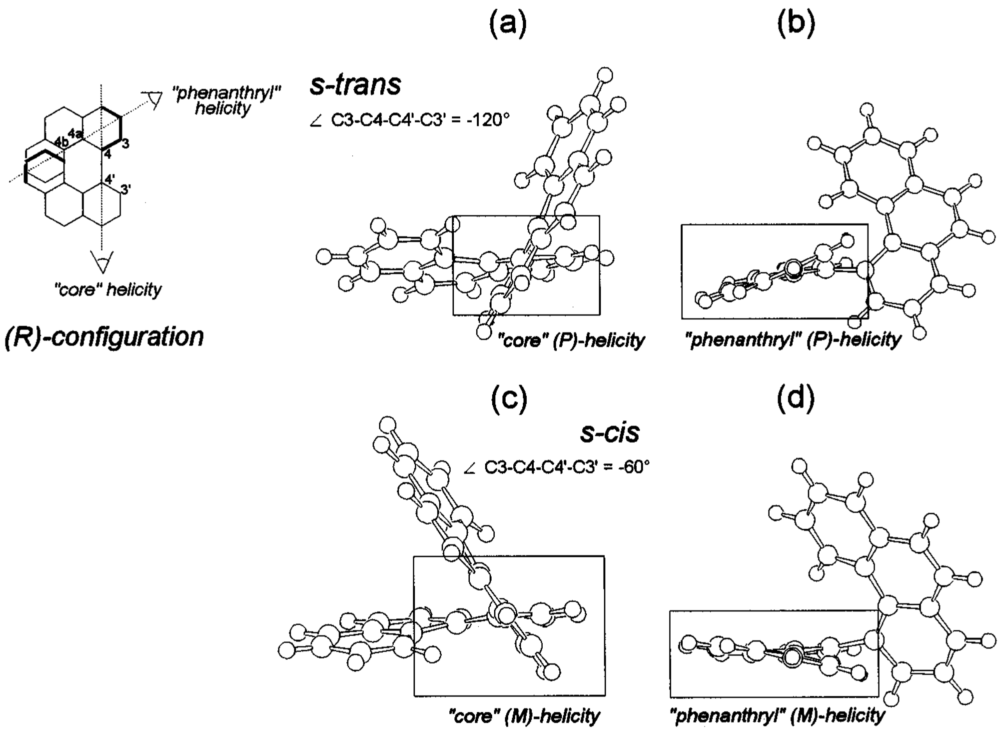

Figure 8. The transfer of helicity from the core to the phenanthryl units in (*R*)-4,4′-biphenanthrene. The *P* helicity in the core along the 4−4′ bond (a) constrains each phenanthryl moiety to become twisted according to *P* helicity along the 4a−4b bond (b). Opposite core helicity (c) induces opposite phenanthryl helicity (d).

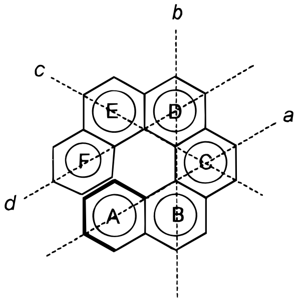

Figure 9.

The present model may explain this aspect: in every case, the dopant presents a twisted chiral surface which is homochiral with the inner helicity. The nematic host experiences *M* helicity of the guest irrespectively of the relative orientation between the solute and solvent molecules.

The fact that the chirality sensed by the nematic solvent is the skewness of a biphenyl unit is confirmed by the analysis of the solvent effect shown in Table 3.

From an inspection of Table 3, it can be noticed that in the bicyclic solvents E7, 1083, and ZLI2359 (“short-core” nematics), compound (*R*)-**2** exhibits twisting powers that are higher than in the nematic solvents MBBA, 1052, and Phase 4 (“long-core” nematics), in which a two-atom spacer is inserted between the two rings. On the other hand, in the case of compound (*M*)-**6**, there is no evident relationship between the structures of the solvent and the solute. The different behavior of the two molecules could be explained as follows in the light of the model discussed above: in the case of (*R*)-**2**, the bicyclic nematics get in close contact with a twisted phenanthryl moiety better than the “long-core” solvents. In the case of (*M*)-**6**, all the nematics have the same ability to fit the continuous twisted ribbonlike compound.

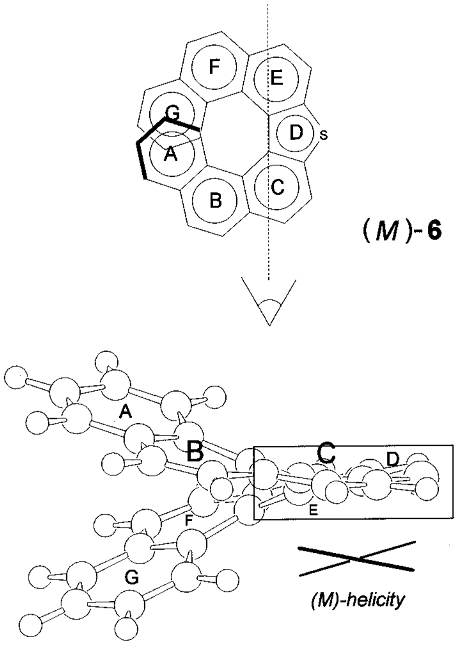

Figure 10. The helicity between the C and D benzene rings in helicene (*M*)-**6**.

Further support to the importance of the conformational equilibrium of the dopant in determining the cholesteric induction phenomenon could be obtained from the observation of the dependence of the pitch on temperature (Figure 11).

In the case of the biphenanthryl derivative (*R*)-**2**, in which temperature may affect the conformational equilibrium, a progressive increase of the pitch with temperature is evident, while in the case of the conformationally locked (*M*)-**6**, the cholesteric pitch does not show any variation with temperature.

Table 3. Twisting Powers of Compounds (*R*)-2 and (*M*)-6 in Different Nematic Solvents

solvent[a]	(*R*)-**2** β (μm^{-1})	(*M*)-**6** β (μm^{-1})
E7	+28	−20
phase 1083	+31	−16
ZLI 2359	+23	−15
MBBA	+9	−20
phase 1052	+15	−30
phase 4	+14	−16

[a] E7: eutectic mixture (from BDH) of 4-cyano-4′-alkylbiphenyl derivatives; Phase 1083: eutectic mixture (from Merck) of 4-(cyanophenyl)-4′-alkylcyclohexane derivatives; ZLI 2359: eutectic mixture (from Merck) of 4-cyano-4′-alkylbicyclohexane derivatives; MBBA: *N*-(4-methoxybenzylidene)-4-butylaniline (from Reidel-de-Haan); Phase 1052: eutectic mixture (from Merck) of 4-pentylphenyl 4′-alkoxybenzoate derivatives; Phase 4: 4-methoxy-4′-butylazoxybenzene derivative (from Merck).

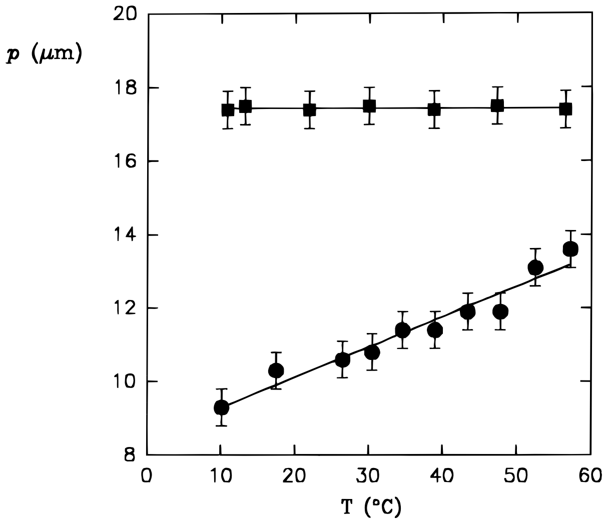

Figure 11. The temperature dependence of the cholesteric pitch of a solution of (*M*)-**6** (■) (*ca.* 2% w/w, ee 20%) and (*R*)-**2** (●) (*ca.* 0.6% w/w) in E7 with temperature.

Conclusions

Circular dichroism spectroscopy and the induction of cholesteric mesophases constitute two powerful and complementary tools to obtain stereochemical information on chiral molecules.

For the open-chain biphenanthryl derivatives **1**−**4**, the exciton split of the ^1B_b transition easily allows the determination of the absolute configuration, in agreement with that obtained *via* chemical correlation. Furthermore, the analysis of the induced cholesterics allows the determination of their conformation: all the open chain derivatives investigated prefer an *s-trans* conformation in agreement with molecular mechanics computations.

Bridged derivative **5**, as well as helicenes **6**−**9**, are conformationally locked; therefore, in principle, by CD spectroscopy, we can obtain the determination (or the confirmation) of the absolute configuration. Unfortunately, however, the differences in the chromophoric characteristics of compounds **5**−**9** prevent an easy correlation of the electronic spectra. On the other hand, the overall shape of these compounds is quite similar, and therefore the liquid crystal technique gives the correct configurational assignment.

The model previously proposed for the cholesteric induction has been extended; it may justify the transmission of chirality from the dopant to the solvent in the case of both classes of compounds **1**−**4** and **5**−**9**. All compounds present twisted surfaces (twisted phenanthryl units or continuous twisted ribbons) that are homochiral with the induced cholesterics as a consequence of the interaction of these surfaces with the solvent molecules.

Experimental Section

Compounds. Synthesis of enantiopure compounds **1**−**5** and of enantiomerically enriched compound **6** was reported in ref 14. Samples of compounds (*M*)-**8** (ee 20%) and (*M*)-**9** were kindly supplied by Professors F. Gasparrini (Rome) and S. F. Mason (London), respectively.

Spectroscopic Measurements. Absorption and circular dichroism spectra were recorded by means of a JASCO V-550 spectrophotometer and a JASCO J-710 spectropolarimeter, respectively. All the spectra were measured at room temperature.

Calculations. The calculations reported here were carried out by means of programs derived from the De Voe treatment according to the procedure described elsewhere.[23]

Induced Cholesteric Measurements. All the nematic phases are commercial products (see caption to Table 3). Cholesteric pitches were measured by means of the "lens" version of the Grandjean−Cano method,[36] using a Standard 16 Zeiss microscope; helical handedness was obtained from the sign of the rotatory power and from the sense of the spirallike disclinations observed under circular boundary conditions.[37] A detailed description of the experiments is reported, for example, in ref 38. Temperature was controlled by means of the thermostated stage Linkam TH 600.

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