Induction of Cholesteric Mesophases by Simple Cyclic Derivatives of *p,p′*-Disubstituted 1,2-Diphenylethane-1,2-diols: Importance of Shape and Polarizability Effects

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A systematic study of the cholesteric induction in nematic solvents (MBBA and E7) by some cyclic derivatives of unsubstituted and *p,p′*-disubstituted-1,2-diphenylethane-1,2-diols shows that the values of the twisting power are significantly dependent on the nature of the link connecting the two oxygen atoms and on the nature of the *p,p′*-substituents. This result has been interpreted considering that the nature of the bridge affects the overall molecular shape and the *p,p′*-substituents affect both the molecular polarizability and shape. This investigation points out that the polarizability of the solute and the solvent is the main parameter in determining the value of the twisting power while electrostatic arene−arene interactions contribute to a less extent. It has been also observed that solutes having the same structure and the same absolute configuration can induce cholesteric helix of opposite sign depending on the substituent on the aromatic ring. This finding indicates that configurational assignments by cholesteric induction are reliable only if high values of twisting power are measured.

Introduction

Induced cholesteric mesophases[1] are interesting and useful optically active materials on account of their stereochemical[1b,2] and technological[3] (e.g., displays) applications. These applications involve induced cholesteric mesophases with definite properties (sense of twist, length of the pitch, etc.) that depend on the structure of the dopant[4] and on the strength of the solute/solvent interactions. A deeper knowledge of the mechanism of induction and of the interactions that determine it is then essential to carry out reliable configurational assignments[2] and to design materials with suitable properties. In addition, since both nematic hosts (e.g., MBBA, K15, etc.) and chiral dopants often bear aromatic rings, a study of the mechanism of cholesteric induction can provide[5] a useful contribution to the understanding of noncovalent arene−arene interactions,[6] a phenomenon that deeply affects the structures and properties of molecular assemblies in biology,[7] chemistry,[8] and material science.[9] We therefore undertook a systematic study aimed at determining the influence of shape and electronic factors onto the cholesteric induction. To this end, the skeleton deriving from 1,2-diphenylethane-1,2-diol has been chosen as chiral template. In fact, (i) 2,2-dimethyl-1,3-dioxolanes derived from 1,2-diarylethane-1,2-diols are efficient inducers of cholesteric mesophases;[10] (ii) this template can give rise to different cyclic, conformationally blocked, derivatives where the shape effects (steric hindrance and molecular size) due to the cycle can be studied; and (iii) electron-donating and electron-withdrawing groups can be easily introduced into the benzene rings, allowing the study of the role played by the nature of the substituent.

In this paper, compounds **2**−**6** (Chart 1) were prepared from the corresponding diols **1a**−**e** and their twisting powers (β_M) measured in the aromatic nematic solvents MBBA (a benzylideneaniline derivative), and E7 (a biphenyl mixture).

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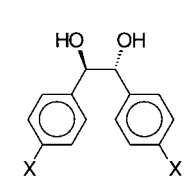
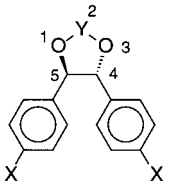
Chart 1

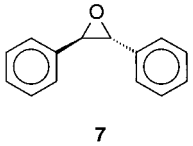


1a-e

a: X = H
b: X = OCH_3
c: X = CH_3
d: X = CF_3
e: X = Cl



2a-e: Y = $C(CH_3)_2$
3a: Y = $CHOCH_3$
4a: Y = CH_2
5a: Y = SO
6a-e: Y = CO



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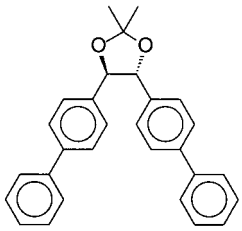

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Synthesis

Compounds **1a**−**c** were prepared as previously described.[10] The new compounds **1d** and **1e** were analogously obtained by catalytic asymmetric dihydroxylation[11] of the corresponding (*E*)-1,2-diarylethenes derived, by McMurry reaction,[12] from 4-trifluoromethylbenzaldehyde or 4-chlorobenzaldehyde. The ee's of diols **1a**−**e** (>90%) were determined by HPLC upon the Daicel Chiralcel OD and OJ columns, and their absolute configurations, assigned as *R*,*R* on the basis of the Sharpless empirical rule,[11] were confirmed by the exciton analysis of the CD spectra of their 2,2-dimethyl-1,3-dioxolanes **2d** and **2e**.[13] The 2,2-dimethyl-1,3-dioxolanes (*R*,*R*)-**2a**−**e** were prepared in high yields (88−97%) by reaction of the corresponding diols (*R*,*R*)-**1a**−**e** and 2,2-dimethoxypropane in $CHCl_3$ in the presence of 4 Å molecular sieves and traces of *p*-TsOH. When (*R*,*R*)-**1a** was reacted with methyl orthoformate in DME and catalytic amounts of *p*-TsOH, (*R*,*R*)-**3a** was obtained, after usual workup and crystallization, in 82% yield.[14] Compound (*R*,*R*)-**4a** was obtained in a 70% yield by reacting (*R*,*R*)-**1a** with CH_2I_2 in CH_2Cl_2, in the presence of KOH and catalytic amounts of 18-crown-6. Reaction of (*R*,*R*)-**1a** with $SOCl_2$ in refluxing CCl_4 provided, after column chromatography, (*R*,*R*)-**5a** in 56% yield.[15] Finally, the carbonates (*R*,*R*)-**5a**−**e** were prepared from the corresponding diols (*R*,*R*)-**1a**−**e** by reaction with triphosgene at −70 °C in the presence of pyridine, in yields ranging from 75 to 85%.[16]

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Table 1. Helical Twisting Powers β_M[a] of Compounds 2a−6a and 7 in the Nematic Solvents MBBA and E7

				β_M (sd)[b]/μm^{-1}	
compd	Y	θ[c] (deg)	d[c] (Å)	in MBBA[d]	in E7[e]
2a	$C(CH_3)_2$	84	5.2	−5.4 (2.0)	−17.8 (3.7)
3a	$CHOCH_3$	88	5.4	−11.9 (0.6)	−21.0 (1.4)
4a	CH_2	79	5.4	−17.7 (0.4)	−30.6 (2.1)
5a	SO	77	5.5	−16.4 (0.2)	−29.9 (0.4)
6a	CO	103	5.9	−22.3 (0.3)	−30.3 (1.4)
7[f]		143	6.4	−37	−32

[a] See ref 17. [b] Standard deviation. [c] From MMX calculations. [d] MBBA: *N*-(4-methoxybenzylidene)-4-butylaniline (from Reidel-de-Haan). [e] E7: eutectic mixture (from BDH) of 4-cyano-4′-*n*-alkylbiphenyl derivatives. [f] Data from ref 19.

Cholesteric Induction

Helical twisting powers, $\beta_M = \pm(pcr)^{-1}$ (where p is the cholesteric pitch, c the molar fraction of the dopant, and r its enantiomeric excess; the sign is taken positive for a right-handed, *P*, cholesteric and negative for a left-handed, *M*, one), have been measured by the Grandjean−Cano method.[17]

The values of β_M of compounds **2**−**6** in the nematic solvents MBBA and E7 are collected in Tables 1 and 2. For the sake of clarity, the discussion will be divided into two parts concerning, respectively, the influence of the ring closure and the effect of the *p*-substituents on the twisting power.

(A) The Role of the Ring Closure. To explain the effects of the structure on the value and sign of β_M (i.e., on the strength of the solute/solvent interactions), the conformation and the geometrical features of the dopant have to be known. The most stable conformations of compounds (*R*,*R*)-**2a**−**6a**, as derived from MMX[18] calculations and previous studies,[10] are shown in Figure 1. In this conformation, the two aromatic rings assume a quasi-gauche relationship when viewed along the C_4−C_5 bond (Figure 1a) and each phenyl nearly bisects the five membered ring (Figure 1b). The nature of the ring junction determines both the steric hindrance around the position 2 of the dioxolane ring and the dihedral angle θ (C_1'−C_4−C_5−C_1'') between the two aromatic rings, thus affecting the distance d between the centers of the phenyl rings. In Table 1 are reported the values of θ, d, and β_M for compounds (*R*,*R*)-**2a**−**6a** and for (*R*,*R*)-*trans*-stilbene oxide (**7**).[19] In these compounds only the type of ring closure is varied, and this structural feature affects mainly the molecular shape (vide supra) even if electronic effects coming from polar moieties (i.e., **5a** vs **4a**) have to be considered. Apparently, the fact that some of these compounds (i.e., **2a**, **4a**, and **6a**) have a C_2 symmetry does not have any influence on the values of β_M measured. The results in Table 1 indicate that, for these unsubstituted derivatives, the sign of β_M is determined only by the handedness of the dopant while its absolute value is significantly affected by the structure of the ring. As a matter of fact, it can be observed that, independently of the nature of the five-membered ring, *R*,*R* derivatives induce a *M* cholesteric, both in MBBA and E7. Molecular

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Table 2. Helical Twisting Powers β_M[a] of Compounds 2a−e and 6a−e in the Nematic Solvents MBBA and E7

				ketals β_M (sd)[b]/μm^{-1}			carbonates β_M (sd)[b]/μm^{-1}		
X	σ_p[c]	α[d]	v[e]		MBBA[f]	E7[g]		MBBA[f]	E7[g]
OCH_3	−0.28	1.31	0.36	**2b**	−11.0 (0.1)	−26.6 (0.8)	**6b**	−38.7 (1.5)	−38.4 (0.1)
CH_3	−0.14	1.23	0.52	**2c**	−18.2 (0.1)	−22.3 (1.7)	**6c**	−29.5 (1.1)	−26.1 (0.7)
Cl	0.24	1.24	0.55	**2e**	−6.22 (0.2)	−22.0 (0.1)	**6e**	−27 (2)	−33.1 (2.3)
H	0	1.04	0	**2a**	−5.4 (2.0)	−17.8 (3.7)	**6a**	−22.3 (0.3)	−30.3 (1.4)
CF_3	0.53	1.16	0.91	**2d**	+9.4 (1.1)	−10.8 (0.2)	**6d**	−20.9 (0.2)	−20.4 (1.1)

[a] See ref 17. [b] Standard deviation. [c] Data from ref 20. [d] Data (10^{-23} cm^3) calculated from Lorenz−Lorentz equation; see ref 5. [e] Data from refs 21 and 22. [f] MBBA: *N*-(4-methoxybenzylidene)-4-butylaniline (from Reidel-de-Haan). [g] E7: eutectic mixture (from BDH) of 4-cyano-4′-*n*-alkylbiphenyl derivatives.

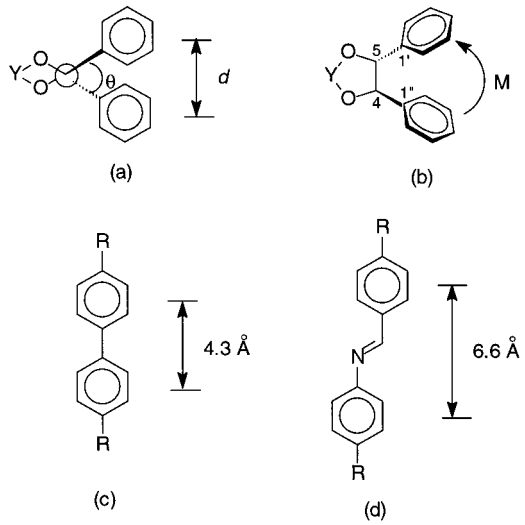

Figure 1. Views of the most stable conformation for derivatives **2**−**6** along the C_4−C_5 bond (a) and from the top (b). θ is the C1′−C4−C5−C1″ dihedral angle. Distances *d* between the aryl cores of a biphenyl (c), taken as a model of E7, and of the MBBA molecule (d).

mechanics calculations[18] indicate that **2a**−**6a** assume[10] prevailing conformations where the benzene rings are *M*-skewed (Figure 1b), thus justifying why they induce, both in the E7 and in the MBBA solvent, *M*-twisted conformations. An interpretation of the different absolute values of β_M observed has, however, to take into account the influence of the Y group onto the overall molecular shape. The trend of β_M values observed in E7 (**2a** < **3a** < **4a** ≈ **5a** ≈ **6a**) can be explained on the basis of the steric hindrance exerted by the group Y. As a matter of fact, in both **2a** and **3a** there is the presence of relatively bulky groups on the 2 position that, being placed out of the plane of the dioxolane ring,[10] can create steric hindrance to the solute/solvent packing. On the other hand, **4a**, **5a**, and **6a** bear, respectively, only two hydrogens or an oxygen on the 2 position, and then steric hindrance to intermolecular solute/solvent interactions is reduced. In MBBA, compounds **2a**−**6a** induce lower values of β_M with respect to E7, indicating less efficient interaction of these substrates with MBBA, and the following trend was observed: **2a** < **3a** < **4a** ≈ **5a** < **6a**. According to the accepted model[2] of cholesteric induction, a close contact between the aromatic moieties of the solute and of the solvent is needed in order to have transmission of chirality. Such a close contact requires a certain degree of similarity between solute and solvent, particularly in shape. This model can then explain[10] why the molecules of *trans*-stilbene oxide (**7**), having a distance *d* between the aryl cores of 6.4 Å (Table 1), interact stronger with the "long" MBBA (d = 6.6 Å, Figure 1c) than with the shorter biphenyl molecules of E7 (d = 4.3 Å, Figure 1d) and why an opposite behavior is shown by the short molecules of the ketals **2a**−**6a** (d < 6 Å). This interpretation can also explain the presently observed trend of β_M in MBBA; in fact, different types of ring closure can determine different kinds of steric hindrance as well as different overall molecular shapes. From Table 1, it is clearly shown that the trend of β_M values is related to the increasing of the interaromatic distances *d* and on the steric hindrance at the 2 position. Lower values of β_M are obtained with the "shorter" molecule **2a** and medium values with **3a**, **4a**, and **5a**. For these compounds, which have very similar values of *d*, the difference in β_M is then determined by the steric hindrance at the position 2, and hence, the less hindered **4a** and **5a** show larger β_M than **3a**. The highest vales are observed with the carbonate **6a** where the presence of a sp^2 CO carbon not only minimizes the hindrance at C_2 but also causes a widening of the θ angle (Table 1), thus lengthening the molecule and increasing its fit with the MBBA molecules. This effect is even more evident with the epoxide **7** which, having the longer *d* and devoid of sterically disturbing groups, shows in MBBA[19] the largest β_M (−37).

As far as the cholesteric induction in E7 is concerned, the difference between the minimum and the maximum β_M is not as high as in MBBA. This is because the biphenyl molecules of E7 are "shorter" than those of MBBA and then there is a better fit with the short molecules of **2a**−**6a**. Therefore, in E7 the lengthening of the molecule disfavors the solute/solvent fit, but the reduction of the steric hindrance still increases the β_M values. The balance of these two factors renders the β_M values less pronounced.

(B) The Role of the *p,p′*-Substituents. In Table 2 are collected the values of the β_M of 2,2-dimethyl-1,3-dioxolanes **2a**−**e** and carbonates **6a**−**e**. The following comments can be made: (i) For the *p,p′*-disubstituted compounds (as for the derivatives **2a**−**6a** discussed above) the correlation (*R,R*)-dopant/*M*-cholesteric also holds, with the sole exception of **2d** in MBBA. (ii) There is a clear effect of the nature of the *p*-substituent on the value of the twisting power. Indeed, electron-donating substituents (see OMe in **2b** and **6b**) induce higher β_M values than electron-withdrawing groups (CF_3), both in the dioxolane and in the carbonate family. (iii) These substituents effects are particularly strong considering that, for instance, in the ketals family passing from **2d** to **2b** the β_M values are more than doubled.

In an attempt to rationalize the experimental facts observed we shall consider that, as shown in the previous paragraph, shape (steric) factors have to be taken into account and that both the electronic nature of the substituents and the polarizability of the systems can

control the β_M values, as recently shown by Williams and Lemieux[5] in a series of substituted chiral biphenyls. In Table 2 are collected the values of the Hammett σ_p constant[20] for the X substituents, which is an index of their electron-donor or -withdrawing character, the Charton parameter (υ),[21] which is related[22] to the steric hindrance of the substituent, and the polarizability values (α) for the corresponding substituted benzenes. We assumed that a measure of the polarizability (α) of **2a**−**e** can be given by the polarizability of the corresponding monosubstituted benzenes calculated by the Lorenz−Lorentz equation.[5]

A satisfactory interpretation of the β_M values observed can be obtained by analyzing their relationship with the polarizability (α) of the substituted phenyl moieties and steric hindrance (υ) of the substituent X of the dopants as reported in Table 2. First, we consider the β_M values of compounds **2a**−**e** (ketals) in the biphenyl nematic solvent E7. The following comments can be easily made: (i) **2c** and **2e** show the same β_M value (within the experimental error), and this result can be explained considering that toluene (model of **2c**) and chlorobenzene (model of **2e**) have the same α values and that the parameters υ for Me and chlorine are very similar. (ii) The highest β_M value recorded for **2b** can be due to the fact that anisole has by far the highest polarizability and the methoxy group has a small steric parameter.[21] (iii) The lowest β_M value is recorded for **2d**; in fact, the polarizability of trifluoromethylbenzene is the lowest in the series (apart from benzene) and the steric requirement of CF_3 is the highest (CF_3 has size and steric parameter υ between a methyl and a *tert*-butyl group).[22,23] (iv) The intermediate β_M value of **2a** is in line with this interpretation, because the small contribution due to the polarizability of benzene is not further reduced by effects due to the size of the substituents.

To further support the above interpretation, it can be observed that (*R*,*R*)-(+)-2,2-dimethyl-4,5-di(4-biphenylyl)-1,3-dioxolane (**8**) (Chart 1) shows in E7[10] a very high β_M value (−58): as a matter of fact, the *p*-phenyl substituent has a small steric parameter, 0.56 (like a methoxy group), but shows a very high group polarizability.[22]

The above interpretation can work also in the case of MBBA where, as for the unsubstituted derivatives, lower values of β_M are obtained (see Table 2). Considering that MBBA and pentylcyano biphenyl (taken as a model of the major component of the E7 mixture) have similar polarizability values (3.15×10^{-23} cm^3 vs 2.91×10^{-23} cm^3) as calculated by the Lorenz−Lorentz equation, the difference in β_M values will depend only on the nature of the solutes.

Unexpectedly, an opposite *P* sign of the cholesteric is induced by the 4-CF_3-substituted ketal (*R*,*R*)-**2d** in MBBA. As already shown in Table 1, ketals (being short molecules) have in MBBA (long molecule) a lower tendency to form *M*-cholesteric than in E7, and as shown in Table 2, the lowest β_M values are obtained with 4-CF_3-substituted compounds. Then it is reasonable that in the case of (*R*,*R*)-**2d** the low tendency to form *M*-cholesteric can be then overwhelmed by the steric hindrance of CF_3

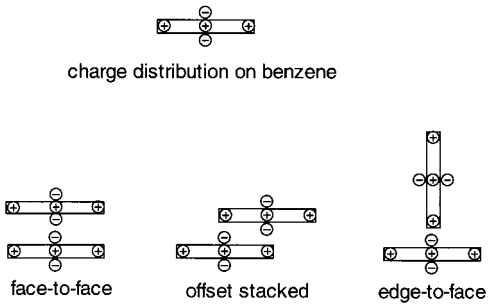

Figure 2. Electrostatic charge distribution on benzene: face-to-face (a), offset stacked (b), and edge-to-face (c) disposition of aromatic moieties.

(as shown above), which can lead to an alternative mechanism of interaction between solute and solvent, giving rise to the opposite sense of twisting of the cholesteric.

The carbonates **6a**−**e** show in E7 higher β values than the ketals **2a**−**e**, and this observation has been previously interpreted considering that carbonates do not possess the steric hindrance of the dimethyl dioxolanes. The behavior of compounds **6a**−**e** in E7 and MBBA can be interpreted as for compounds **2a**−**e**. Interestingly, in this case we do not observe any inversion of the cholesteric helix: reasonably, compounds (*R*,*R*)-**6** interact so strongly with the nematic solvent to give an *M* cholesteric that steric effects are not able to overwhelm this tendency.

The analysis reported above agrees with the original mechanism of cholesteric induction proposed by Gottarelli et al.,[2,24] who, assuming π-facial interactions between the aromatic moieties of dopant and solvent, state that the sense of twist of the aromatic moieties of the dopant is responsible for the sense of the cholesteric induction. We showed that other factors such as polarizability and overall molecular shape strongly contribute to the determination of the value of the twisting power. The role played by the polarizability of the solute seems to indicate that attractive dispersive forces may contribute (in addition to hard-core repulsive interaction)[25] to the cholesteric induction; however, since we are dealing with aromatic solvents and solutes, arene−arene interactions cannot be ruled out, and then it is also interesting to analyze the present experimental data taking into account the models describing arene−arene interactions. Some recent experimental[6d,e] and theoretical[6a−c,f] studies have in fact shown that these interactions are mainly of electrostatic nature and that the benzene ring has a charge distribution showing a negative potential above and below the molecular plane and a positive potential focused on the carbon skeleton and on the hydrogens (Figure 2).[6a,7] According to this electrostatic model, face-to-face (a) aromatic dispositions are then disfavored, maximizing π electron repulsion, while shifted, or offset stacked (b), and edge-to-face (c) orientations, which face the positively charged σ-framework and the negatively charged π-electrons are stabilized. By examining the possibilities of interaction of the aromatic moieties of solutes **2** and **6** with the phenyl rings of a biphenyl

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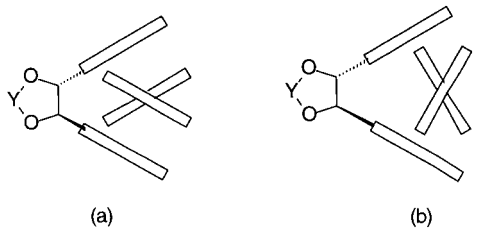

Figure 3. Possible dispositions of the aromatic moieties of solutes **2** and **6** with a biphenyl.

solvent such as E7, the two dispositions in Figure 3 can be depicted. Orientation (a) in Figure 3, with the biphenyl molecule shifted in respect to the arenes of the solute, is compatible with an offset-stacked disposition of the aromatic rings, while orientation (b) ensures a stabilizing edge-to-face orientation of the aromatic moieties. It has to be noted that with both these orientations a *R,R* dopant molecule, whose benzene rings define an *M* chirality, induce an *M*-twisted conformation in the biphenyl molecule (compare dispositions (a) and (b) in Figure 3). This electrostatic model can also explain the trend of β_M values reported in Table 2, which increases with the electron-donor properties of the substituent onto the aromatic ring of the dopant. As a matter of fact, according to the edge-to-face or the offset-stacked model, the electrostatic arene−arene attraction increases with an increase of the electron density on the arene borne by the dopant.[6c] The chlorine-substituted compounds **2e** and **6e** constitute a significant exception to this model because the values of β_M are higher than those expected only on the basis of the σ_p value of chlorine. This result can be only explained by taking into account also the high polarizability of Cl (vide supra). This finding, then, further confirms that the above interpretation based on polarizability effects and on the intervention of dispersive forces affords a more complete explanation of the experimental results. The interpretation based on the polarizability effects also agrees with the experimental finding that ketals **2b**, **2d**, and **2e** show, in the nonaromatic solvent ZLI2359, β_M values of −22.7, −24.9, and −14.8 μm^{-1}, respectively, comparable with those obtained in the aromatic nematics MBBA and E7. In this case, arene−arene interactions are clearly not involved, while only the intervention of dispersive forces can explain the high β_M values, considering the high polarizability (2.06×10^{-23}) showed by dicyclohexyl (i.e., the structural moiety of the component of ZLI2359).

Conclusions

In conclusion, this investigation has confirmed that the twisting power β_M *is a function of the overall molecular shape* (the solvent molecules recognize the distortion of the solute, and they feel whether the solute is "long" or "short" and if something on the solute surface blocks their fit) and has demonstrated that *a substituent, affecting the electronic properties (i.e., polarizability*[26] *and electron density) and the steric requirements of the parent compound, can heavily affect the* β_M *values*. The effect of substituents has been interpreted on the basis of their contribution to the molecular polarizability, thus pointing out the role played by dispersive forces on the chirality transfer from the solute to the nematic solvent. Taking into account the aromatic structure of both the solutes and the solvents tested, it has been also pointed out that arene−arene electrostatic interactions can contribute, even if to a lesser extent, to afford an efficient cholesteric induction. These two types of interactions (i.e., polarization and electrostatic) are somehow connected as the substituents, affecting the electron density on the aromatic ring, influence both the polarizability and the charge distribution of the arenes. The importance of the substituent effects is demonstrated also by the observation that solutes having the same absolute configuration but different substitution can induce cholesteric with opposite sign (see ketals in MBBA). This observation clearly points out that reliable configurational correlations based on the analysis of the cholesteric induction are achievable only with solutes affording high values of β_M. To obtain a safe configurational correlation, it is then necessary to choose suitable derivatives of the compounds studied, similar in shape to the molecules of solvent, so that high β_M values result, independently of the nature of the substituents (the case of the carbonates **6a**−**e** is a clear example). The findings reported herein can have important consequences from both theoretical (formulation of quantitative models of cholesteric induction,[27] understanding of the factors determining solute/solvent interactions) and practical points of view (rational design of chiral liquid crystal materials for technological applications).

Experimental Section

General Procedures. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$. Enantiomeric excesses of the diols were determined by HPLC analysis on a Daicel Chiralcel OD or Chiralcel OJ column. CCl_4 and CH_2Cl_2 were distilled, respectively, from CaH_2 and P_2O_5 and stored over activated 4 Å molecular sieves. Analytical and preparative TLC were performed, respectively, on 0.2 and 2.0 mm silica gel plates Merck 60 F-254, and column chromatography was carried out with silica gel Merck 60 (80−230 mesh). Enantiomerically pure (*R,R*)-1,2-diarylethane-1,2-diols **1a**−**e** were prepared by catalytic asymmetric dihydroxylation[11] of the corresponding *p,p′*-disubstituted-(*E*)-stilbenes obtained, in turn, from Wittig reaction or McMurry coupling.[12] Dioxolanes **2a**−**c** were prepared as previously described.[10] *N*-(4-Methoxybenzylidene)-4-butylaniline (MBBA) (Reidel-de-Haan) and E7 mixture (BDH) were used as purchased.

General Procedure for the Synthesis of 4,5-Diaryl-2,2-dimethyl-1,3-dioxolanes. To a solution of (*R,R*)-1,2-diarylethane-1,2-diol (0.14 mmol) in $CHCl_3$ (5 mL) was added 2,2-dimethoxypropane (0.172 mL, 1.4 mmol), followed by traces of *p*-toluensulfonic acid and activated 4 Å molecular sieves. The mixture was stirred at room temperature overnight and then filtered over a short pad of silica gel (eluent $CHCl_3$). The solvent was evaporated to recover a solid residue of pure dioxolane.

(*R,R*)-(+)-4,5-Di(4-trifluoromethylphenyl)-2,2-dimethyl-1,3-dioxolane (2d): yield 95%; mp 74−76 °C; $[\alpha]_D = +54.9$ ($c = 0.65$, $CHCl_3$); ^{1}H NMR δ 1.70 (s, 6H), 4.75 (s, 2H), 7.34 (d, $J = 8.1$ Hz, 4H), 7.60 (d, $J = 8.1$ Hz, 4H); ^{13}C NMR δ 27.03, 84.81, 110.33, 125.50, 126.95, 130.60, 131.05, 140.49; MS (EI)

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m/*z* 216 (M^+, 100), 159 (67), 147 (79). Anal. Calcd for $C_{19}H_{16}F_6O_2$: C, 58.47; H, 4.13. Found: C, 58.23; H, 4.41.

(*R*,*R*)-(+)-4,5-Di(4-chlorophenyl)-2,2-dimethyl-1,3-dioxolane (2e): yield 85%; mp 101−102 °C; $[\alpha]_D = +113.2$ (*c* = 1.4, $CHCl_3$); ^{1}H NMR δ 1.66 (s, 6H), 4.63 (s, 2H), 7.12 (d, *J* = 8.5 Hz, 4H), 7.30 (d, *J* = 8.5 Hz, 4H); ^{13}C NMR δ 27.11, 84.84, 109.74, 127.96, 128.73, 134.23, 134.97. Anal. Calcd for $C_{17}H_{16}Cl_2O_2$: C, 63.17; H, 4.99. Found: C, 63.31; H, 4.72.

(*R*,*R*)-(+)-4,5-Diphenyl-2-methoxy-1,3-dioxolane (3a). The diol (*R*,*R*)-**1** (100 mg, 0.47 mmol) was dissolved in DME (3 mL), and then trimethyl orthoformate (51 μL, 0.47 mmol) and traces of *p*-TsOH were added at room temperature. The mixture was stirred for 1 h and then diluted with Et_2O, washed with saturated $NaHCO_3$ (aq) and brine, and dried over Na_2SO_4. After evaporation of solvent, a solid residue was recovered that was recrystallized from CH_2Cl_2−petroleum ether, obtaining 102 mg (85%) of **3a** as white crystals: mp 106−107 °C; $[\alpha]_D = +76.6$ (*c* = 2.39, $CHCl_3$); ^{1}H NMR δ 3.53 (s, 3H), 4.82 (d, *J* = 8.6 Hz, 1H), 4.97 (d, *J* = 8.6 Hz, 1H), 6.12 (s, 1H), 7.33 (m, 10H). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.77; H, 6.41.

(*R*,*R*)-(+)-4,5-Diphenyl-1,3-dioxolane (4a). To a solution of (*R*,*R*)-**1** (200 mg, 0.93 mmol) in CH_2Cl_2 (10 mL) were added in sequence 18-crown-6 (25 mg, 0.093 mmol), finely ground KOH (210 mg, 3.72 mmol), and CH_2I_2 (300 μL, 3.72 mmol). The mixture was stirred overnight at room temperature and then diluted with CH_2Cl_2, washed twice with water and brine, and dried over anhydrous Na_2SO_4. After evaporation of solvent, the residue was purified by column chromatography (3:1 petroleum ether/Et_2O) to obtain 168 mg (80% yield) of **4a** as a white solid: mp 51−52 °C; $[\alpha]_D = +82.2$ (*c* = 1.04, $CHCl_3$); ^{1}H NMR δ 4.71 (s, 2H), 5.47 (s, 2H), 7.33 (m, 10H); ^{13}C NMR δ 85.42, 96.37, 126.49, 128.31, 128.56, 137.52; MS (EI) *m*/*z* 226 (M^+, 2), 120 (100), 91 (52). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.58; H, 6.32.

(*R*,*R*)-(+)-4,5-Diphenyl-1,3,2-dioxatiolan-2-one (5a).[15,28] To a suspension of (*R*,*R*)-**1** (200 mg, 0.93 mmol) in CCl_4 (5 mL) was added $SOCl_2$ (83 μL, 1.12 mmol) under nitrogen atmosphere. The mixture was then refluxed for 1 h and cooled at room temperature and the solvent evaporated. The solid residue obtained was purified by column chromatography over silica gel (petroleum ether/Et_2O = 3:1) to obtain 198 mg (82%) of **5a** as a white solid: mp 98−100 °C; $[\alpha]_D = +148$ (*c* = 0.68, $CHCl_3$); ^{1}H NMR δ 5.22 (d, *J* = 9.5 Hz, 1H), 5.70 (d, *J* = 9.5 Hz, 1H), 7.45 (m, 10H); ^{13}C NMR δ 86.15, 91.45, 127.40, 127.76, 129.13, 129.54, 129.85, 132.47, 133.53.

General Procedure for the Synthesis of 4,5-Diaryl-1,3-dioxolanones. A solution of 1,2-diarylethane-1,2-diol (0.14 mmol) and pyridine (0.24 mL, 0.84 mmol) in CH_2Cl_2 (3 mL) was cooled at −70 °C, and a solution of triphosgene (42 mg, 0.14 mmol, 1 equiv) in anhydrous CH_2Cl_2 (2 mL) was added. The mixture was then allowed to warm at room temperature, stirred overnight, and then washed with saturated NH_4Cl (aq) and the aqueous phase extracted with CH_2Cl_2. The collected organic phases were washed with 10% aqueous HCl and with saturated $NaHCO_3$ (aq) and then dried over anhydrous Na_2SO_4. After evaporation of solvent, the collected residue was purified by column chromatography.

(*R*,*R*)-(+)-4,5-Diphenyl-1,3-dioxolanone (6a):[29] yield 85%; mp 110−112 °C (for (±)-**6a** lit.[30] mp 110−111 °C); $[\alpha]_D = +66$ (*c* = 1.05, $CHCl_3$); ^{1}H NMR δ 5.45 (s, 2H), 7.4 (m, 10H); ^{13}C NMR δ 85.34, 126.05, 129.23, 129.78, 134.88, 154.02.

(*R*,*R*)-(+)-4,5-Di(4-methoxyphenyl)-1,3-dioxolanone (6b): yield 78%; $[\alpha]_D = +144.7$ (*c* = 1.05, $CHCl_3$); ^{1}H NMR δ 3.83 (s, 6H), 5.37 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 4H), 7.23 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 55.28, 85.34, 114.48, 126.33, 127.78, 154.08, 160.63. Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.13; H, 5.28.

(*R*,*R*)-(+)-4,5-Di(4-methylphenyl)-1,3-dioxolanone (6c): yield 82%; $[\alpha]_D = +105.7$ (*c* = 1.2, $CHCl_3$); ^{1}H NMR δ 2.38 (s, 6H), 5.33 (s, 2H), 7.19 (d, *J* = 8.3 Hz, 4H), 7.23 (d, *J* = 8.3 Hz, 4H); ^{13}C NMR δ 21.22, 85.45, 126.12, 129.81, 131.76, 139.80, 154.22. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.95; H, 6.23.

(*R*,*R*)-(+)-4,5-Di(4-trifluoromethylphenyl)-1,3-dioxolanone (6d): yield 70%; mp 58−60 °C; $[\alpha]_D = +47$ (*c* = 1.06, $CHCl_3$); ^{1}H NMR δ 5.45 (s, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.74 (d, *J* = 8.2 Hz, 4H); ^{13}C NMR δ 84.28, 125.36, 126.44, 132.11, 132.56, 138.16, 153.17. Anal. Calcd for $C_{17}H_{10}F_6O_3$: C, 54.27; H, 2.68. Found: C, 54.43; H, 2.82.

(*R*,*R*)-(+)-4,5-Di(4-chlorophenyl)-1,3-dioxolanone (6e): yield 77%; mp 70−71 °C; $[\alpha]_D = +114.7$ (*c* = 2.91, $CHCl_3$); ^{1}H NMR δ 5.36 (s, 2H), 7.24 (d, *J* = 8.4 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H);^{13}C NMR δ 84.59, 127.46, 129.57, 132.75, 136.07, 153.42. Anal. Calcd for $C_{15}H_{10}Cl_2O_3$: C, 58.28; H, 3.26. Found: C, 58.17; H, 3.41.

Induced Cholesteric Measurements. Cholesteric pitches were measured by means of the "lens" version of the Grandjean−Cano method, using a standard 16 Zeiss microscope; helical handedness was obtained from the sign of the rotatory power and from the sense of the spiral-like disclination observed under circular boundary conditions.[17c]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **2d**, **2e**, **3a**, **4a**, **5a**, **6a**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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