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A Study of the Stereochemistry of 2-Aryl-4,5-dimethyl-1,3-dioxolanes by Cholesteric Induction in Nematic Phases and Circular Dichroism Spectroscopy

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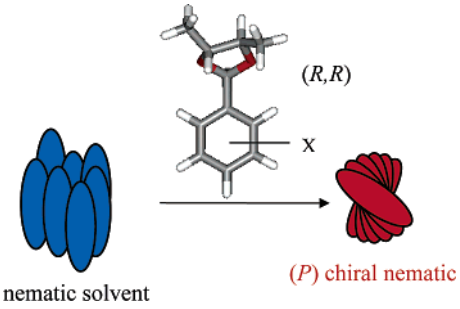

The circular dichroism spectra and the twisting ability of a series of 2-aryl-4,5-dimethyl-1,3-dioxolanes used as dopants in nematic solvents have been related to their absolute configuration. Whereas the circular dichroism (CD) spectra are deeply affected by the substituents present in the aromatic ring, which in several cases cause sign inversion, the helical twisting power β is only marginally influenced. The values of β also seem not very sensitive to the rotamer population around the aromatic ring; this indicates the predominant importance of the chiral dioxolane ring in determining the cholesteric induction. These facts can be explained by the different nature of the two observables: in CD, the chirality is read by the absorbing chromophore and is deeply influenced even by small changes of this group. In cholesteric induction we are dealing instead with chiral solute−solvent interactions that determine a twist in the solvent. In light of the present and previous results, this process seems predominantly determined by short-range interactions, which are modulated by the molecular shape. From a practical point of view, a configurational correlation using CD for the present series of compounds seems problematic, while the values of β are nicely correlated to the absolute configurations. Calculations with the surface chirality method predict well the sign and order of magnitude of β and their limited sensitivity to the phenyl substituents and rotamer population.

Introduction

The fact that doping nematic phases with chiral nonracemic compounds transforms them into chiral nematic (cholesteric) phases has been known for a long time.[1] This chiral induction is a process by which the molecular chirality is mapped onto a nematic by inducing a helical spatial arrangement of the nematic director; chiral nematics of opposite handedness are induced by enantiomers. The ability of a dopant to torque a nematic phase is called "helical twisting power" (β) and is numerically expressed in eq 1:

$$\beta = (pcr)^{-1} \quad (1)$$

where p is the helical pitch, c is the dopant concentration, and r is its enantiomeric excess; the sign of β is taken as positive for right-handed (P) induced chiral nematics.[2,3]

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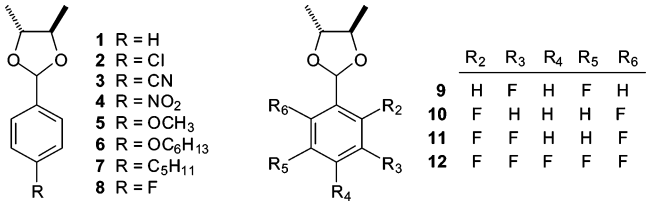
One interesting aspect of the chiral doping of nematic phases is the possibility to use this phenomenon to assess the absolute configuration of chiral solutes[4,5] as an alternative to classical chiroptical techniques.[6]

The handedness and pitch of induced chiral nematic phases are determined by the coupling of the chirality and orientational behavior of the dopants. Therefore, the relation between the configuration of the dopant and the sense of the phase is neither simple nor obvious,[7] but some empirical rules correlating the stereochemistry of the dopant to the handedness of the phase have been derived from experimental observations.[4,8] A general use of the technique would require the understanding of the molecular mechanism at the origin of the chiral induction.

The phenomenon of chiral induction originates from the torque exerted by the chiral probe on the local nematic director, which is transmitted at a distance by virtue of the elastic properties of the liquid crystalline phase. The magnitude and sign of β depends in a subtle way, for a given solvent, on the structure of the solute, and even small changes in the chemical nature of substituents can affect it. A quantitative relation between β and the molecular structure of the chiral dopant can be theoretically derived by the surface chirality model, which accounts for the *short-range solute−solvent interactions modulated by the solute molecular shape*.[9,10] The model rests on the assumption that the anisotropy and chirality of such interactions, which determine the twisting ability of the dopant, can be parametrized on the basis of the anisometry and helicity of the molecular surface. Other theoretical approaches as well as atomistic and nonatomistic simulations have been proposed for the calculation of the helical twisting power of dopants.[11]

With the help of the surface chirality method, the absolute configuration of different classes of compounds has been assessed from the helical twisting powers measured in nematic phases: axially chiral compounds such as helicenes,[12] biphenyl,[13] binaphthyl derivatives,[14] and compounds displaying simple central chirality such as sulfoxides.[15]

CHART 1



	R_2	R_3	R_4	R_5	R_6
9	H	F	H	F	H
10	F	H	H	H	F
11	F	F	H	H	F
12	F	F	F	F	F

Helical twisting power is a sensitive probe of the anisotropy and chirality of solute−solvent interactions. Actually, it has been found that often solvent can be simply considered as an orienting and elastic medium, whose macroscopic properties, rather than specific structure, affect the twist of the induced cholesteric phase. Therefore, cholesteric induction can be explained on the basis of the molecular features of the dopant, without the need of an explicit account of the structure of solvent. However, in some cases dramatic solvent effects have been observed, comprising the change of cholesteric handedness when a given dopant is dissolved in different nematics.[15] Noncovalent interactions between aromatic rings might have some responsibility in this kind of behavior. Such interactions are known to play an important role in stabilizing biological structures, organic supramolecules, and nanomaterials,[16] and many articles have appeared recently on the nature of these interactions and on the substitution effect.[17] In particular, Lemieux and co-workers have used liquid crystalline media to investigate the role of arene−arene interactions.[18]

In this article, we consider the series of 2-aryl-4,5-dimethyl-1,3-dioxolanes **1**−**12**, which present homochiral structures but different substitutions in the aromatic ring (Chart 1). Our aim is to see if the substituent electronic effect is probed by the nematic phase or, on the contrary, if the chiral transfer is dominated by the shape of the solute. With the purpose of investigating the possible effects of interactions between aromatic rings, helical twisting power has been measured in two nematic solvents similar in shape, but one having a biphenyl and the other a bicyclohexyl core. Also, circular dichroism (CD) spectra have been recorded to compare the effect of substituents on two different chiral properties of solutes (i.e., their ability in twisting a nematic solvent and the differential absorption of circularly polarized light).

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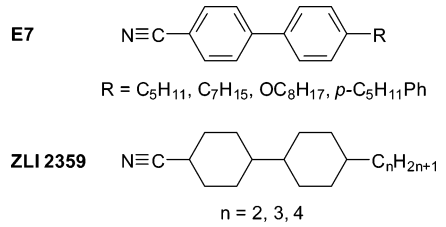
TABLE 1. Helical Twisting Powers β of Derivatives 1−12 in the Nematic Solvents E7 and ZLI 2359 at Room Temperature

	β (μm^{-1})	
compound	E7	ZLI2359
1	+6.1	+4.7
2	+7.1	+7.5
3	+5.6	+6.6
4	+5.1	+5.8
5	+9.6	+8.5
6	+10.3	+8.7
7	+8.2	+7.2
8	+5.5	+6.5
9	+4.0	+4.4
10	+4.9	+5.8
11	+5.2	+7.7
12	+4.7	+6.7

CHART 2



Results and Discussion

Cholesteric Induction. Derivative **1** was chosen as the parent compound because it presents a stereogenic fragment (the 1,3-dioxolane unit) with a C_2 symmetry. This requirement has been found to enhance the helical twisting power with respect to similar compounds with C_1 symmetry.[4] The presence of the substituents will modify the electronic density in the phenyl rings. In particular, perfluoro substitution inverts the sign of its quadrupolar moment.[16]

The helical twisting powers of (*R*,*R*)-**1**−**12**, reported in Table 1, were measured in two commercially available solvents, one aromatic and the other aliphatic, selected for their similarity in shape: E7 is an eutectic mixture of cyanobiphenyl (and terphenyl) compounds while ZLI2359 is an eutectic mixture of cyanobicyclohexyl derivatives (see Chart 2).

From the data reported in Table 1, it appears that all compounds with (*R*,*R*) configuration induce right-handed cholesterics in both nematic phases. Small differences are observed between the two solvents, which do not support the presence of a discriminating role of arene−arene interactions. The absolute values of β are relatively small ($\beta \leq 10$ μm^{-1}), as expected for small molecules with central chirality and do not change a great deal with the substituents (there is a factor of 2.5 between the highest and the smallest value). Although the different substituents exhibit quite different electronic effects (with σ_p Hammet constants ranging from −0.28 for CH_3O to +0.81 for NO_2)[19] and modify the dopant polarizability to a different extent (NO_2 and OCH_3 being much more effective than F),[18] values of β of the *same sign* and similar magnitudes are constantly observed; this seems to indicate that the electronic character is not the main feature in controlling the chiral transfer between solute and solvent.

The importance of the molecular shape as the main factor controlling the helical twisting power of the compounds under investigation is confirmed by calculations based on the surface chirality model. The theoretical model has been presented in detail elsewhere,[9,10] and only some aspects are reviewed here. The value of β of a given dopant in a nematic solvent can be calculated by eq 2:

$$\beta = a\boldsymbol{Q} \tag{2}$$

Here Q is the chirality parameter and a is a factor that depends on the solvent properties; it is defined as $a = RT\xi/2\pi K_{22}\nu_m$, where R and T are the gas constant and the temperature, ξ, K_{22}, and ν_m are the orienting strength, the twist elastic constant, and the molar volume of the solution, respectively. The chirality parameter $\boldsymbol{Q}$ is a property of the dopant, which depends on the coupling of its *chirality and orientational* behavior. In fact, it can be expressed in terms of the *ordering* $\boldsymbol{S}$ and *helicity* $\boldsymbol{Q}$ tensors:

$$\boldsymbol{Q} = -\sqrt{(^2/_3)}\,(\boldsymbol{Q}_{xx}\boldsymbol{S}_{xx} + \boldsymbol{Q}_{yy}\boldsymbol{S}_{yy} + \boldsymbol{Q}_{xx}\boldsymbol{S}_{yy}) \tag{3}$$

The ordering tensor, whose elements S_{ii} give the degree of alignment to the local director of the correspondent *i*-molecular axes, is in turn obtained from a molecular tensor $\boldsymbol{T}$. The $\boldsymbol{Q}$ and $\boldsymbol{T}$ tensors are calculated by exploring the molecular surface by normal unit vectors; the components T_{ii} and Q_{ii} quantify, respectively, the anisometry and the helicity of the molecular surface, as viewed along the *i*-axis (for the physical meaning and significance of the tensors $\boldsymbol{S}$, $\boldsymbol{Q}$, and $\boldsymbol{T}$, see the Experimental Section). The dopant is modeled as an assembly of van der Waals spheres centered at the atomic position; the molecular surface is then defined as the envelope drawn by a sphere rolling over the assembly.[20] It follows from the definition that the chirality parameter Q depends on the molecular geometry; in the case of flexible dopants, it changes with the molecular conformation.

Equation 2 allows a direct comparison between measured twisting powers and chirality parameters calculated for different dopants in a given nematic solvent. Using reasonable estimates[12] (i.e., $T \approx 300$ K, $K_{22} \approx 3 \times 10^{-12}$ N, $\nu_m \approx 3 \times 10^{-4}$ m^3, $\xi \approx 3 \times 10^{-2}$ Å^{-2}), we obtained a value of the order of the unity for the a factor, if β and Q are expressed in μm^{-1} and in Å^3, respectively.

The molecular geometry of the dioxolane derivatives was obtained by DFT calculations at the B3LYP/6-31G** level;[21] torsional profiles were obtained by relaxed scan minimization. Figure 1 shows the potential energy as a function of the H−C−C_{Ar}−C_{Ar} dihedral angle for derivatives **1** and **10**. The presence of para or meta substituents does not significantly affect the torsional profiles; namely, the results obtained for compounds **8**, **9**, and **1** are very similar. The energy minimum for derivatives *without* ortho-substituents (compounds **1**−**9**) is characterized by a dihedral angle H−C−C_{Ar}−C_{Ar} of about 85° (geometry I); a second, shallow minimum, 1.7 kJ mol^{-1} higher, is centered at about 0° (geometry II). In the presence of

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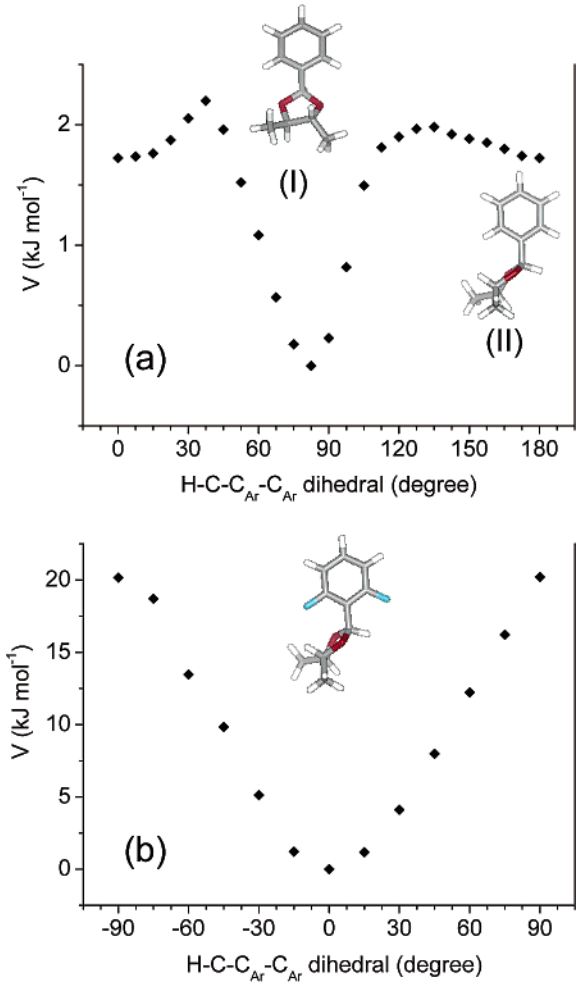

FIGURE 1. H−C−C_{Ar}−C_{Ar} torsional potential calculated for compound **1** (a) and **10** (b). The molecular structures represent the conformation at the minima.

TABLE 2. Chirality Parameters Q Calculated for Compounds 1−5 and 8−12: Conformers I and II Refer to the Geometry Shown in Figure 1

	Q (Å^3)	
compound	conformer I	conformer II
1	+1.0	+3.25
2	+1.6	+3.35
3	+2.1	+3.2
4	+1.7	+4.7
5	+2.05[a]	+3.55[a]
8	+1.4	+3.35
9	+0.8	+4.45
10	=	+2.7
11	=	+3.15[b]
12	=	+3.8

[a] Average of the two possible geometries with OCH_3 coplanar with the phenyl ring. [b] Average of the two conformers obtained by a 180° rotation of the phenyl ring.

substituents in the ortho position (compounds **10**−**12**), geometry I is strongly hindered and only conformation II, with the phenyl ring almost bisecting the O−C−O angle (H−C−C_{Ar}−C_{Ar} of about 0°), is practically significant.

In Table 2, the chirality parameters Q calculated for compounds **1**−**5** and **8**−**12** are reported (in this analysis derivatives **6** and **7** have not been considered due to the presence of a long and flexible tail that complicates the conformational analysis). For compounds **1**−**9**, the contribution of the two conformers I and II is reported. For the reasons explained earlier, only geometry II has been considered in the case of compounds **10** and **12**. Positive chirality parameters are obtained for the minimum energy conformations of all derivatives.

The general agreement in sign and magnitude between Q values and β measurements confirms that the twisting ability of the dioxolane derivatives under investigation is mainly determined by the molecular shape, with electronic effects playing a minor role. A closer inspection of the data reported in Table 2 shows that the predicted Q values generally are higher in the presence of bulky susbstituents. No relation between experimental β values and dimension of substituents appears in Table 1, which shows a more complex dependence on the nature of the substituents. We can take as an example derivatives **4** and **5**. Rather high Q values are calculated for both, which can be explained by the presence of bulky substituents; on the contrary, the measured twisting power is relatively low for the former and high for the latter. The discrepancy between predictions and experiments probably reflects electronic effects, which are not taken into account by the surface chirality model and are expected to contribute in an opposite sense in the case of electron-donating and -withdrawing substituents. The small but nonnegligible magnitude of such contributions and their dependence on the electronic nature of substituents were assessed for substituted biphenyls[13] using a more sophisticated modeling, taking into account electrostatic interactions.

On the basis of the analysis of the experimental β values, a simple and naïve illustration (Figure 2) can explain why an (*R*,*R*) dopant induces a (*P*)-cholesteric. The model assumes that (i) only short-range intermolecular interactions are responsible for the twist induction (experimentally observed in this series of compounds), (ii) the chirality transfer is similar in the stable conformations (confirmed by computation), and (iii) the molecular axis of preferential alignment with the local director can be predicted (in this series the compounds present an axis of maximum elongation). With these assumptions, the dopant molecule is aligned with its long axis more or less parallel to the rodlike molecules of the solvent; however, the (*R*,*R*)-stereogenic fragment disturbs the parallel alignment and imposes the correct (*P*)-twist that leads to the helicoidal arrangement. This kind of

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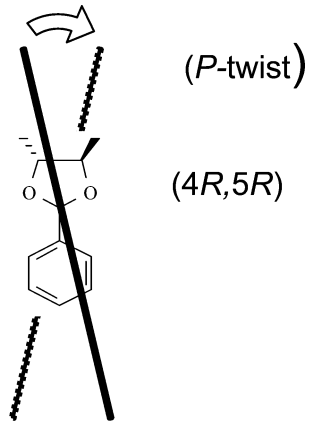

FIGURE 2. Simplified model to predict the twist sense induced by an (*R*,*R*)-dopant.

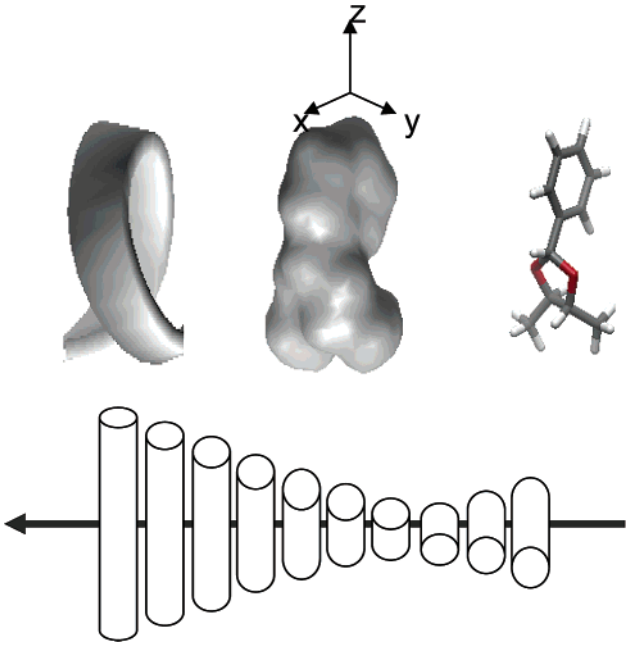

FIGURE 3. Top: molecular surface of (*R*,*R*)-**1** in the geometry with the phenyl ring perpendicular to the dioxolane moiety. The (*x*,*y*,*z*) axes are parallel to the principal axes of the ***S*** ordering tensor; the right-handed helicity of the surface along the *y* direction clearly appears. Bottom: right-handed helical deformation of the nematic director.

simplified model has already been used in the past to assign the configuration of a few series of compounds.[22]

The analysis of the molecular surface by means of the surface chirality model leads to the same result as that shown in Figure 2. As a didactic example, the molecular surface of (*R*,*R*)-**1** in the geometry with the phenyl ring perpendicular to the dioxolane moiety is reported in Figure 3. For this geometry, the elements of the ordering tensor ***S*** are $S_{xx} = -0.08$, $S_{yy} = -0.17$, $S_{zz} = 0.25$, and the corresponding values of the ***T*** and ***Q*** tensors are $T_{xx} = -7$ Å^2, $T_{yy} = -25$ Å^2, $T_{zz} = 32$ Å^2, and $Q_{xx} = -49$ Å^3, $Q_{yy} = 48$ Å^3, $Q_{zz} = 1$ Å^3. From the ordering tensor we infer that this molecule orients its *z*-axis parallel ($S_{zz} > 0$) and its *y*-axis perpendicular ($S_{yy} < 0$) to the director; since the surface has a right-handed helicity along the *y* axis ($Q_{yy} > 0$), a director deformation to form a right-handed cholesteric helix is predicted.

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TABLE 3. CD Features, λ and $\Delta\epsilon$, of the B_{2u} Transition of the Benzene Chromophore for the (*R*,*R*)-1−8

compound	λ/nm ($\Delta\epsilon/10^{-2}$)
1	266.5 (−1.9); 260.5 (−3.5); 255 (−4.3)
2	272.7 (−2.51); 265.5 (−2.67)
3	278 (−8.3); 270.5 (−7.9)
4	254 (−27)
5	280.5 (+8.2); 274 (+9.0)
6	280.2 (+8.2); 274.4 (+9.3)
7	269.7 (−2.5); 264.7 (−3.8)
8	269.5 (+5.9); 263 (+5.9)

Circular Dichroism. Because a series of homogeneous compounds with similar conformations and different ring-substituents was available, we measured also their CD spectra; in fact, the problem of substituent effect on the CD spectra of aromatic compounds has been tackled by several research groups without achieving a simple interpretation.[23]

We will limit the discussion to only the benzene-like B_{2u} transition, because high-energy transitions are not accurately measured for compounds with a small *g* factor ($\Delta\epsilon/\epsilon$), as for the present compounds. We will also not undertake a vibrational analysis,[24] which is beyond the scope of the present work.

The data for compounds **1**−**8** are reported in Table 3. We have considered only para-substituted compounds because ortho-substituents affect the conformation and render the discussion too complex; the same is true for polysubstituted compounds.

In the literature,[23] the interpretation of the CD spectra related to the benzene-like B_{2u} transition is focused on two possible mechanisms: "vibronic" and "inductive". The CD intensity is the sum of the two independent contributions.

In the "vibronic" contribution, the CD intensity is borrowed from transitions at higher energy by means of vibrations; this mechanism seems dominant for benzenes with a stereogenic center attached to the ring and without other ring substituents.

The "inductive" contribution becomes important when other ring substituents are present and contribute to increase the absorption intensity; it is connected to the spectroscopic moment of the substituents.[25] For *p*-substituted derivatives, when the substituent has a positive spectroscopic moment (OH: +34, OCH_3: +31, F: +21, CH_3: +7, Cl: +6, Br: +4),[26] the inductive contribution is opposite to the vibronic one, and consequently a sign inversion can be observed. Instead, substituents with a negative spectroscopic moment (CN, CF_3) give contributions consignate with the vibronic one.

(23) For a comprehensive review, see: Smith, H. E. In *Circular Dichroism, Principles and Applications*; Berova, N., Nakanishi, K., Woody, R. W., Eds; Wiley-VCH: New York, 2000; Chapter 14.

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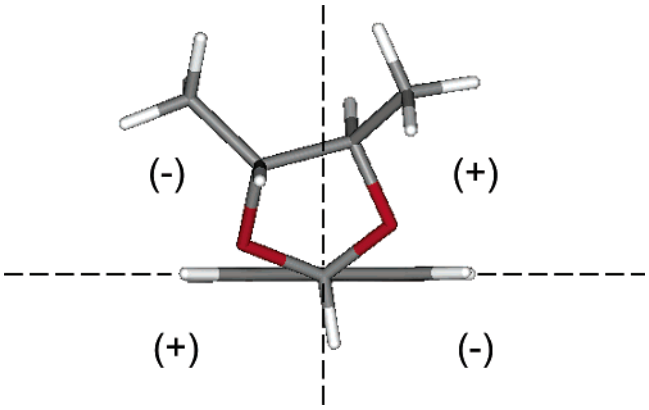

FIGURE 4. Sign contribution to the CD of the B_{2u} transition according to the quadrant sector rule of monosubstituted benzenes.[23] The molecular structure is shown in the more stable conformer I.

A quadrant sector rule was proposed for the vibronic contribution based on the two symmetry planes of a monosubstituted benzene. From the calculations reported above, the compounds considered here have a similar dominant conformation and the achiral *p*-substituents do not seem to affect the conformation reported in Figure 4. The molecules have groups belonging to the chiral dioxolane moiety almost equally distributed in opposite sectors, and it does not seem sensible to use the sector rule in the present case; the only possible prediction is that the CD must be as weak as it is experimentally (Table 3).

The data on *p*-Cl-substituted derivative **2** is somehow disturbing because it is consignate with the unsubstituted derivative and has very similar intensity. Because Cl has a positive spectroscopic moment, one should expect a sign inversion or strong reduction of intensity; however, one could argue that Cl has the smallest positive moment among the substituents studied here and that the vibronic contribution is dominant. Data on OCH_3, OR, and F substituents show instead the expected sign inversion, while the CN substituent is consignate with the unsubstituted compound.

We can conclude that, for the present series of compounds, the CD of the B_{2u} transition cannot be used safely to correlate the absolute configurations using the models presently available.

Conclusions

While the CD spectra are deeply affected by the substituents present in the aromatic ring, which, in several cases, cause sign inversion, the helical twisting power is only marginally influenced; even the perfluoro derivative **12** displays β values similar to the other derivatives. The values of β seem also not very sensitive to the rotamer population around the aromatic ring; this indicates the predominant importance of the chiral dioxolane ring in determining the cholesteric induction.

These facts can be explained by the different nature of the two observables: in CD, the chirality is read by the absorbing chromophore (in the present case the aromatic ring) and is deeply influenced even by small changes of this group. In cholesteric induction we are dealing instead with chiral solute−solvent interactions that determine a twist in the solvent. In light of the present and previous results, this process seems predominantly determined by short-range intermolecular interactions. Even the pentafluoro substituted compound does not show any relevant interaction with the aromatic liquid crystal.[27]

From a practical point of view, a configurational correlation using CD for the present series of compounds seems problematic while the values of β are nicely correlated to the absolute configurations.

Calculations with the surface chirality method predict well the sign and order of magnitude of β and its limited sensitivity to the phenyl substituents. The predominant importance of short-range interactions is also confirmed.

Experimental Section

CD spectra in hexane solution were recorded at room temperature.

Cholesteric Induction Experiments. Cholesteric pitch and handedness have been obtained at room temperature using the lens version of the Grandjean−Cano method.[28] The standard error of the pitch determination is ca. 10%. The technique is described in detail in ref 29. Eutectic mixtures used as nematic solvents are commercial products: E7, T_i = 60 °C; ZLI 2359, T_i = 68°C.

Synthesis. For the preparation of derivatives (*R*,*R*)-**1**-**12**, the general procedure described by Patel et al.[30] was followed. NMR spectra were recorded either on a 200 MHz or on a 300 MHz spectrometer. Chemical shifts are given in ppm. ^{13}C NMR assignments were confirmed by DEPT experiments. Mass spectra were obtained at 70 eV (EI).

(*R*,*R*)-4,5-Dimethyl-2-phenyl-1,3-dioxolane (1). The crude reaction mixture was purified by column chromatography on silica (eluant petroleum ether/ethyl ether, 8:2). The title compound (R_f 0.45) was obtained as a colorless oil in a 43% yield. Spectral data were identical to those reported by Kurihara and Hakamata.[31]

(*R*,*R*)-2-(4-Chlorophenyl)-4,5-dimethyl-1,3-dioxolane (2). The product was obtained as a colorless oil in a 35% yield after column chromatography on silica gel (eluant petroleum ether/ethyl ether, 97:3) (R_f 0.53); ^1H NMR ($CDCl_3$) δ 1.33 (3H, d, J = 6.04 Hz), 1.38 (3H, d, J = 5.81 Hz), 3.71−3.89 (2H, m), 5.92 (1H, s), 7.32−7.47 (4H,m); ^{13}C NMR ($CDCl_3$) δ 16.8 (CH3), 17.1 (CH_3), 78.7 (CH), 80.4 (CH), 101.8 (CH), 127.9 (CH), 128.5 (CH), 134.8 (C), 137.2 (C); MS *m*/*z* 212 [M^+], 211, 139, 89, 56; $C_{11}H_{13}ClO_2$ (212.68) Calcd: C, 62.12; H, 6.16. Found: C, 62.41; H, 6.39.

(*R*,*R*)-2-(4-Cyanophenyl)-4,5-dimethyl-1,3-dioxolane (3). The title compound was isolated as a white solid in a 88% yield by column chromatography on silica (eluant petroleum ether/ethyl ether, 8:2) (R_f 0.46); ^1H NMR ($CDCl_3$) δ 1.34 (3H, d, J = 5.93 Hz), 1.37 (3H, d, J = 5.93 Hz), 3.69−3.91 (2H, m), 5.97 (1H, s), 7.57−7.71 (4H, m); ^{13}C NMR ($CDCl_3$) δ 16.8 (CH_3), 17.0 (CH_3), 78.8 (CH), 80.6 (CH), 101.3 (CH), 112.7 (C), 118.6 (C), 127.2 (CH), 132.2 (CH), 143.9 (C); MS *m*/*z* 147 [$M^+ - C_4H_8$], 134, 119, 91; $C_{12}H_{13}NO_2$ (203.24) Calcd: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.87; H, 6.29; N, 7.06.

(*R*,*R*)-4,5-Dimethyl-2-(4-nitrophenyl)-1,3-dioxolane (4). The title compound was isolated as a white solid in a 42% yield by column chromatography on silica (eluant petroleum ether/

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ethyl ether, 8:2) (R_f 0.49); ^{1}H NMR ($CDCl_3$) δ 1.35 (3H, d, J = 5.91 Hz), 1.39 (3H, d, J = 5.91 Hz), 3.70−3.93 (2H, m), 6.02 (1H, s), 7.64−7.70 (2H, m), 8.21−8.27 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.8 (CH_3), 17.0 (CH_3), 78.9 (CH), 80.6 (CH), 101.1 (CH), 123.6 (CH), 127.4 (CH), 145.8 (C), 184.4 (C); MS *m/z* 223 [M^+], 89, 77, 56; $C_{11}H_{13}NO_4$ (223.23) Calcd: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.00; H, 5.67; N, 6.25.

(*R*,*R*)-2-(4-Methoxyphenyl)-4,5-dimethyl-1,3-dioxolane (5). The product was obtained as a colorless oil in a 84% yield after column chromatography on silica gel (eluant petroleum ether/ethyl ether, 8:2) (R_f 0.49); ^{1}H NMR ($CDCl_3$) δ 1.33 (3H, d, J = 5.93 Hz), 1.39 (3H, d, J = 5.93 Hz), 3.74−3.88 (5H, m, s), 5.91 (1H, s,), 6.87−6.95 (2H, m), 7.39−7.46 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.9 (CH_3), 17.2 (CH_3), 55.3 (CH_3), 78.5 (CH), 80.3 (CH), 102.5 (CH), 113.7 (CH), 127.8 (CH), 130.8 (C), 160.3 (C); MS *m/z* 208 [M^+], 207, 135, 108, 77; $C_{12}H_{16}O_3$ (208.26) Calcd: C, 69.21; H, 7.74. Found: C, 69.25; H, 7.59.

(*R*,*R*)-2-(4-Hexyloxyphenyl)-4,5-dimethyl-1,3-dioxolane (6). The reaction mixture was purified by column chromatography on silica (eluant petroleum ether/ethyl ether, 9:1). The title compound (R_f 0.34) was obtained as a colorless oil in a 57% yield; ^{1}H NMR (DMSO-d_6) δ 0.88 (3H, t, J = 7.0 Hz), 1.23 (3H, d, J = 5.7 Hz) 1.26−1.46 (9H, d, m), 1.65−1.74 (2H, m), 3.66−3.77 (2H, m), 3.96 (2H, t, J = 7.0 Hz), 5.80 (1H, s), 6.88−6.93 (2H, m), 7.30−7.35 (2H, m); ^{13}C NMR (DMSO-d_6) δ 13.8 (CH_3), 16.8 (CH_3), 17.1 (CH_3), 22.0 (CH_2), 25.1 (CH_2), 28.6 (CH_2), 30.9 (CH_2), 67.4 (CH_2), 77.9 (CH), 79.4 (CH), 101.6 (CH), 114.0 (CH), 127.9 (CH, s), 130.7 (C), 159.4 (C); MS *m/z* 278 [M^+], 277, 121, 94; $C_{17}H_{26}O_3$ (278.39) Calcd: C, 73.35; H, 9.41. Found: C, 73.49; H, 9.11.

(*R*,*R*)-4,5-Dimethyl-2-(4-pentylphenyl)-1,3-dioxolane (7). Purification of the crude reaction mixture by column chromatography on silica gel (eluant petroleum ether/ethyl ether, 9:1) afforded the desired product (R_f 0.35) as a colorless oil in a 60% yield; ^{1}H NMR (DMSO-d_6) δ 0.79−0.92 (3H, t), 1.18−1.4 (10H, m), 1.49−1.62 (2H, m), 2.48−2.65 (2H, t), 3.62−3.81 (2H, m), 5.81 (1H, s), 7.12−7.38 (4H, m); MS *m/z* 248 [M^+], 91, 77, 56; $C_{16}H_{24}O_2$ (248.37) Calcd: C, 77.38; H, 9.74. Found: C, 77.32; H, 9.88.

(*R*,*R*)-2-(4-Fluorophenyl)-4,5-dimethyl-1,3-dioxolane (8). The compound was obtained as a colorless oil in a 58% yield after column chromatography on silica gel (eluant petroleum ether/ethyl ether, 9:1) (R_f 0.48); ^{1}H NMR ($CDCl_3$) δ 1.32 (3H, d, J = 5.7 Hz), 1.38 (3H, d, J = 5.8 Hz), 3.71−3.88 (2H, m), 5.91 (1H, s), 6.99−7.11 (2H, m), 7.41−7.51 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.9 (CH_3), 17.2 (CH_3), 78.7 (CH), 80.4 (CH), 102.0 (CH), 115.2 (d, CH, J = 21.5 Hz), 128.4 (d, CH, J = 8.3 Hz), 137.1 (d, C, J = 6.3 Hz), 162.3 (d, C, J = 252.7 Hz); MS *m/z* 196 [M^+], 195, 123, 108, 56; $C_{11}H_{13}FO_2$ (196.22) Calcd: C, 67.33; H, 6.68. Found: C, 67.30; H, 6.47.

(*R*,*R*)-2-(3,5-Difluorophenyl)-4,5-dimethyl-1,3-dioxolane (9). The crude reaction mixture was purified by column chromatography on silica (eluant petroleum ether/ethyl ether, 8:2). The title compound (R_f 0.46) was obtained as a colorless oil in a 78% yield; ^{1}H NMR ($CDCl_3$) δ 1.32 (3H, d, J = 5.8 Hz), 1.36 (3H, d, J = 5.7 Hz), 3.67−3.87 (2H, m,), 5.89 (1H, s), 6.72−6.83 (1H, m), 6.95−7.07 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.8 (CH_3), 16.9 (CH_3), 78.7 (CH), 80.5 (CH), 101.0 (t, CH, J = 2.5 Hz), 104.2 (t, CH, J = 25.4 Hz), 109.1−109.6 (m, CH), 143.1 (t, C, J = 8.4 Hz), 163.0 (dd, C, J = 250.0, 12.4 Hz); MS *m/z* 214 [M^+], 213, 155, 141, 56; $C_{11}H_{12}F_2O_2$ (214.21) Calcd: C, 61.68; H, 5.65. Found: C, 61.87; H, 5.38.

(*R*,*R*)-2-(2,6-Difluorophenyl)-4,5-dimethyl-1,3-dioxolane (10). The product was obtained as a colorless oil in a 70% yield after column chromatography on silica gel (eluant petroleum ether/ethyl ether, 8:2) (R_f 0.49); ^{1}H NMR ($CDCl_3$) δ 1.33 (3H, d, J = 6.11 Hz), 1.41 (3H, d, J = 5.98 Hz), 3.71−3.99 (2H, m), 6.37 (1H, s), 6.81−6.95 (2H, m), 7.22−7.37 (1H, m); ^{13}C NMR ($CDCl_3$) δ 16.1 (CH_3), 16.9 (CH_3), 78.6 (CH), 80.8 (CH), 95.6 (t, CH, J = 4.9 Hz), 111.5−112.1 (m, CH), 114.8 (t, C, J = 14.5 Hz), 130.9 (t, CH, J = 10.5 Hz), 161.7 (dd, C, J = 252.6, 7.4 Hz); MS *m/z* 214 [M^+], 141, 126, 63, 56; $C_{11}H_{12}F_2O_2$ (214.21) Calcd: C, 61.68; H, 5.65. Found: C, 62.13; H, 5.74.

(*R*,*R*)-2-(2,3,6-Trifluorophenyl)-4,5-dimethyl-1,3-dioxolane (11). Purification of the crude reaction mixture by column chromatography on silica gel (eluant petroleum ether/ethyl ether, 98:2) afforded the desired product (R_f 0.32) as a colorless oil in a 94% yield; ^{1}H NMR ($CDCl_3$) δ 1.33 (3H, d, J = 5.97 Hz), 1.41 (3H, d, J = 5.86 Hz), 3.71−3.99 (2H, m), 6.35 (1H, s), 6.76−6.89 (1H, m), 7.06−7.22 (1H, m); ^{13}C NMR ($CDCl_3$) δ 16.0 (CH_3), 16.8 (CH_3), 78.8 (CH), 80.9 (CH), 95.3−95.5 (m, CH), 110.7−111.4 (m, CH), 116.5−117.1 (m, C), 117.5−118.0 (m, CH), 144.6−145.0 (m, C), 146.6−147.0 (m, C), 149.4−149.9 (m, C), 151.6−152.1 (m, C), 154.0−154.4 (m, C), 159.0−159.5 (m, C); MS *m/z* 232 [M^+], 188, 159, 144; $C_{11}H_{11}F_3O_2$ (232.20) Calcd: C, 56.90; H, 4.77. Found: C, 56.58; H, 4.95.

(*R*,*R*)-2-(Pentafluorophenyl)-4,5-dimethyl-1,3-dioxolane (12). The reaction mixture was purified by column chromatography on silica (eluant petroleum ether/ethyl ether, 98:2). The title compound (R_f 0.35) was obtained as a colorless oil in a 69% yield; ^{1}H NMR ($CDCl_3$) δ 1.33 (3H, d, J = 5.94 Hz), 1.40 (3H, d, J = 5.94 Hz), 3.71−3.96 (2H, m), 6.31 (1H, s); ^{13}C NMR ($CDCl_3$) δ 15.9 (CH_3), 16.8 (CH_3), 79.0 (CH), 81.0 (CH), 94.9−95.3 (m, CH), 112.5−113.1 (m, C), 134.7−135.4 (m, C), 139.2−139.3 (m, C), 139.9−140.3 (m, C), 142.9−143.2 (m, C), 144.1−144.5 (m, C), 147.9−148.4 (m, C); MS *m/z* 268 [M^+], 224, 195, 180, 161; $C_{11}H_9F_5O_2$ (268.18) Calcd: C, 49.27; H, 3.38. Found: C, 49.69; H, 3.35.

Calculations. Optimized geometries and potential energy profiles are obtained by DFT calculation at the B3LYP/6-31G**.[21] The chirality parameter ***Q*** is calculated with a homemade code, based on the following procedure:[9,10] (1) Given the nuclear positions, the molecular surface is generated. This is defined as the surface drawn by the center of a bead rolling on the assembly of van der Waals spheres centered on the nuclei and is approximated by a set of triangles, obtained with the algorithm developed by Sanner et al.[20] (2) The ***T*** and ***Q*** tensors, related respectively to the anisometry and the chirality of the molecular surface, are calculated by summing the contributions from all the triangles. (3) The elements of the Saupe ordering matrix ***S*** are calculated as averages over all molecular orientations:

$$S_{ij} = \frac{\int \mathrm{d}\phi \exp[-U(\phi)/k_B T]\left(\frac{3}{2}\cos\varphi_i \cos\varphi_j - \frac{1}{2}\right)}{\int \mathrm{d}\phi \exp[-U(\phi)/k_B T]} \quad (4)$$

where φ denotes the angles between the molecular axes (i,j) and the local director, and $U(\varphi)$ is the orienting potential experienced by the molecule in the nematic phase:

$$\frac{U(\phi)}{k_B T} = -\sqrt{\frac{3}{2}}\sum_{i,j} T_{ij} \cos\varphi_i \cos\varphi_j \quad (5)$$

Finally, the chirality parameter Q is obtained according to eq 3. The results reported in Table 2 have been obtained giving the parameter ξ the value 0.03 Å^{-2} and the rolling sphere radius the value 3 Å. The following van der Waals radii are used: r_O = 1.5 Å, r_O = 1.85 Å, r_F = 1.35 Å, r_{Cl} = 1.8 Å, r_N = 1.5 Å, $r_{H\ (alkyl)}$ = 1.2 Å, $r_{H\ (aromatic)}$ = 1 Å.

All principal values of the ***T*** tensor would vanish for a spherically symmetric surface. Nonvanishing components indicate deviations from the spherical symmetry along the corresponding directions; a positive (negative) value is obtained if the surface is elongated (flatted) along a given axis. Thus, for example, a prolate ellipsoid or a rod is characterized by a positive ***T*** component along the C_∞ axis, and two negative components perpendicular to it. The orienting potential experienced by a molecule in the nematic phase can be parametrized in terms of the ***T*** tensor; according to eq 5 such a

potential is lowest when the direction of maximum elongation (greatest $\boldsymbol{T}$ component) is aligned to the director. The ordering tensor $\boldsymbol{S}$ is calculated from eq 4. The elements of this tensor express the degree of alignment of the molecule ($-0.5 \leq S_{ii} \leq 1$);[32] a large positive value along an axis corresponds to a high degree of alignment, while a large negative value indicates that the axis tends to lie perpendicular to the director.

The $\boldsymbol{Q}$ tensor components describe the helicity of the surface, as viewed along the reference axes. A positive (negative) component corresponds to a right-handed (left-handed) helicity. A given surface can have different helicities, depending on the direction probed. When a molecule is dissolved in a nematic phase, the helicity transferred to the medium depends on its average orientation.

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