# Conformational Analysis of Some *trans*-4,5-Diaryl-1,3-dioxolanes by CD Spectroscopy and Induction of Cholesteric Mesophases in Nematic Solvents: A Correlation between Twisting Power and Structure of the Dopant

**Carlo Rosini,\*,† Gian Piero Spada,\*,‡ Gloria Proni,‡ Stefano Masiero,‡ and Simone Scamuzzi§**

*Contribution from the Università della Basilicata, Dipartimento di Chimica, via N. Sauro 85, 85100 Potenza, Italy, Università di Bologna, Dipartimento di Chimica Organica "A. Mangini", via S. Donato 15, 40127 Bologna, Italy, and Università di Pisa, CNR-CSMSOA, Dipartimento di Chimica e Chimica Industriale, via Risorgimento 35, 56126 Pisa, Italy*

*Received July 16, 1996*⊗

**Abstract:** A series of *trans*-4,5-diaryl-1,3-dioxolanes (compounds **1**−**10**) has been prepared from the corresponding 1,2-diols obtained by asymmetric *syn*-dihydroxylation of (*E*)-olefins, in the presence of derivatives of quinidine. Compounds **1**−**10**, when dissolved in MBBA or E7, induce left-handed cholesterics, showing twisting powers which, in absolute value, are strongly dependent on the structure of the solute and on the nature of the nematic mesophase. By means of molecular mechanics calculations and the analysis of CD spectra of **1**−**10**, it is possible to determine the most stable conformation of these derivatives which is characterized by a negative twist of the aryl moiety. With this information a reliable cholesteric induction model has been developed.

## Introduction

Modern techniques of configurational assignment[1] (analysis of circular dichroism (CD) spectra, of cholesteric mesophases induced in nematic liquid crystals, and of the elution order upon chiral stationary phases (CSP) for HPLC) have been recently employed[2] to characterize several 1,2-diarylethane-1,2-diols after their transformation into the corresponding 4,5-diaryl-1,3-dioxolanes, *i.e.*, derivatives that are rigid and nonassociated and whose molecular conformation is more reliably determinable than that of the starting compounds. Both the analysis of the CD spectra and of the induced cholesteric mesophases have been previously[2] carried out at a qualitative level; in particular, the cholesteric mesophases have been characterized only by recognizing the handedness (*P* or *M*) of the cholesteric helix. A better understanding of the ability of a chiral dopant to twist the nematic phase is given by its twisting power[3] $\beta = 1/(pcr)$, where p is the cholesteric pitch, c the molar fraction of solute, and r its enantiomeric excess. The sign of $\beta$ is taken as positive for right-handed (*P*) cholesteric phases and negative for left-handed (*M*) ones. The twisting power (and its sign) is sensitive to the molecular shape, and it has been extensively applied to stereochemical studies.[4,5] Furthermore, the recent presentation by Nordio and co-workers[6] of a theoretical model for calculation of the magnitude and the handedness of helical pitch in terms

of molecular shape anisotropy of the dopant opens new perspectives for configurational assignments by the liquid crystals technique. We decided to undertake a more detailed analysis of the cholesteric induction ability of these dioxolanes by measuring the twisting powers of compounds **1**−**13** in two different nematic solvents and investigating in detail the induction mechanism for two main reasons: first of all, only a knowledge of the correct induction mechanism can allow a reliable correlation between the helicity of the cholesteric and the absolute configuration of the dopant; second, this knowledge could help in the design of some 4,5-diaryl-1,3-dioxolane dopants to induce chiral mesophases with interesting technological applications.[7] This paper describes also a quantitative analysis of the CD spectra of such derivatives which, together with some molecular mechanics calculations, provide a detailed description of the molecular conformation of the chiral solute, a fundamental piece of information required to formulate a reliable cholesteric induction mechanism.

## Results and Discussion

**Synthesis.** Compounds **1**−**3** and **5**−**10** have been prepared and characterized as previously described[2] by asymmetric *syn*-dihydroxylation of some (*E*) olefins in the presence of quinidine derivatives, providing the corresponding dextrorotatory 1,2-diols. By treatment with 2,2-dimethoxypropane/TsOH they have been

† Università della Basilicata.
‡ Università di Bologna.
§ Università di Pisa.
⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1996.
(1) Eliel, E. L.; Wilen, S. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1993.
(2) Rosini, C.; Scamuzzi, S.; Pisani Focati, M.; Salvadori, P. *J. Org. Chem.* **1995**, *60*, 8289.
(3) Gottarelli, G.; Spada, G. P.; Solladié, G. *Nouv. J. Chim.* **1986**, *10*, 691. Gottarelli, G.; Spada, G. P. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 377. Solladié, G.; Zimmermann, R. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348.
(4) Gottarelli, G.; Hibert, M.; Samorì, B.; Solladié, G.; Spada, G. P.; Zimmermann, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7318.

(5) Gottarelli, G.; Spada, G. P.; Bartsch, R.; Solladié, G.; Zimmermann, R. *J. Org. Chem.* **1986**, *51*, 589. Gottarelli, G.; Spada, G. P.; Seno, K.; Hagishita, S.; Kuriyama, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1607. Arnone, C.; Gottarelli, G.; Spada, G. P.; Spinelli, D.; Exner, O. *J. Mol. Struct.* **1986**, *147*, 307. Naciri, J.; Spada, G. P.; Gottarelli, G.; Weiss, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4352. Suchod, B.; Renault, A.; Lajzerowicz, J.; Spada, G. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1839. Rosini, C.; Franzini, L.; Salvadori, P.; Spada, G. P. *J. Org. Chem.* **1992**, *57*, 6820. Rosati, I.; Rosini, C.; Spada, G. P. *Chirality* **1995**, *7*, 353. Gottarelli, G.; Proni, G.; Spada, G. P.; Fabbri, D.; Gladiali, S.; Rosini, C. *J. Org. Chem.* **1996**, *61*, 2013.
(6) Ferrarini, A.; Moro, G. J.; Nordio P. L. *Mol. Phys.* **1996**, *87*, 485.
(7) Jang, K.; Lemieux, R. P. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 247.

**Chart 1**
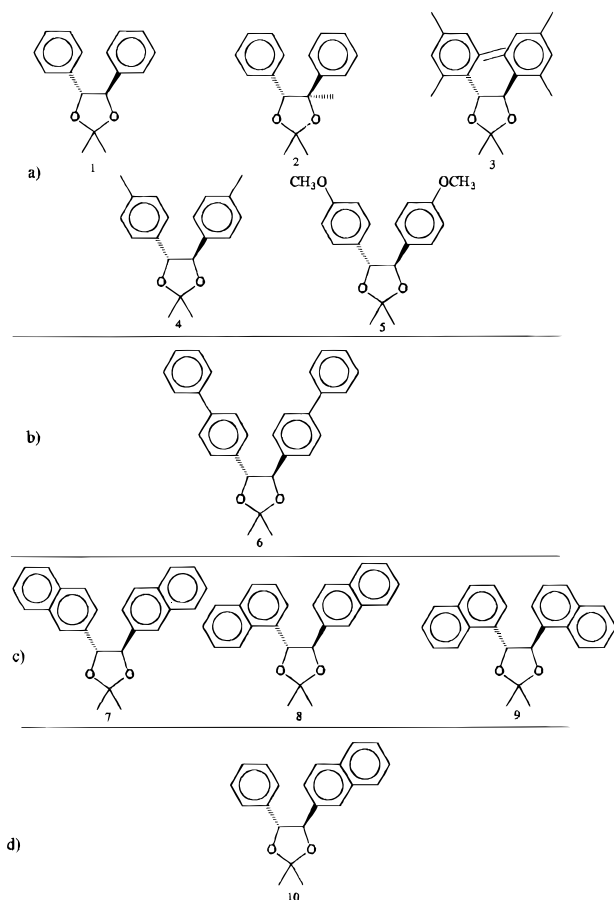


transformed into the corresponding dioxanes, to which the (*R,R*) absolute configuration has been assigned.[2] Compound **4** has been analogously prepared (in excellent yield and enantiomeric excess (ee)) and characterized starting from (*E*)-4,4′-dimethylstilbene. Compounds **11** and **12** (Chart 3) were prepared[8] from (*E*)- and (*Z*)-β-methylstyrene, respectively. It is interesting to note that while the *syn*-dihydroxylation of the (*E*) olefin affords the diol in 95% ee, the same reaction carried out on the (*Z*)-olefin affords the diol in 33% optical yield only.

**Circular Dichroism.** From a spectroscopic point of view, the molecules studied possess aromatic chromophores (substituted benzene, biphenyl, and naphthalene), whose electronic transitions are fully characterized,[9] whence a nonempirical interpretation of the CD allied to these transitions can be certainly attempted. In order to simplify the description of the chiroptical properties of compounds **1**–**10**, we have classified them in four different classes (see Chart 1): (a) those containing the substituted benzene chromophore only (**1**–**5**); (b) compounds with the biphenyl chromophore (**6**); (c) compounds containing the naphthalene chromophore (**7**–**9**); (d) compounds containing two different chromophores (**10**).

Table 1 collects the most relevant absorptions and CD features of compounds **1**–**10**. In Figure 1 are reported the absorption and CD spectra of **3**, which can be considered as representative of class a. The absorption spectrum shows a band at 200 nm ($\epsilon = 68\,000$) due to the electrically allowed $\pi$–$\pi^*$, which, in the underivatized benzene chromophore, is labeled as $^1A_{1g} \rightarrow {}^1E_{1u}$, and a clear shoulder ($\epsilon = 15\,000$) at 222 nm related to the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition. In the CD spectrum, one can observe

the $^1A_{1g} \rightarrow {}^1B_{1u}$ Cotton effect at 234 nm ($\Delta\epsilon = +28$) and a positive couplet[10] centered at 200 nm having the positive maximum at 208 nm ($\Delta\epsilon = +100$) with the negative one at 196 nm, $\Delta\epsilon = -66$. Also the 220-nm Cotton effect may be assigned to a positive couplet originating from the coupled oscillator system[10] formed by the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition: only the positive branch of the couplet is evident as a consequence in part of a cancellation effect operated by the more intense couplet centered around 190 nm and, in part, of the configuration interaction.[11] It is noteworthy that the compounds **1**, **2**, and **4**, which are electronically very similar to **3** (the only difference in these compounds being the amount of methyl substitution), show CD spectra which are very similar to each other and to the CD spectrum of **3**. In particular, the 220-nm Cotton effect has an intensity of about +20 in all the derivatives. They all show a positive couplet at about 190 nm, which derives from the coupled oscillator system[10] constituted by the $^1A_{1g} \rightarrow {}^1E_{1u}$ electronic transition of the substituted benzene chromophores. The intensity of this couplet is quite similar in the molecules (the amplitudes are +111 for **1**, +156 for **2**, +166 for **3**, and +92 for **4**). The intensity of an exciton couplet depends on several factors:[12] the intensity of the transitions of the monomeric chromophore and on the relative disposition of the two chromophores. In a case like the present one where the chromophores are very similar (an alkyl-substituted benzene ring), the geometrical factors (conformation of the dioxane ring and rotation around the C*–Ar bond) should play an important role so that the intensity of the couplet could be a probe of the overall molecular conformation. The similar values recorded for **1**–**4** are a strong indication of very similar conformation of these compounds.

The higher intensity observed for **3** (Figure 1) and **2** (Table 1) could be related to a larger conformational homogeneity for these compounds (this seems to be very reasonable: the methyl group in **2** and the *o,o*-methyl groups in **3** guarantee a restricted rotation around the C*–Ar bond). The examination of molecular (Dreiding) models of dioxanes having (*R,R*) configurations reveals some interesting aspects. In fact, the dioxane ring can assume the two limit conformations reported in Chart 2.

Structures **a** and **b** differ in the value of the dihedral angle Ar–C*–C*–Ar (~90° in A and ~180° in B). In structure B the Ar groups are quite near the 2,2-methyl groups of the dioxane ring, giving rise to steric hindrance. This is particularly true in the case of **3** where the *o*-methyl groups increase noticeably the size of Ar. These simple considerations have been fully supported by molecular mechanics calculations (MMX routine[13]), performed on a few derivatives, for which the (*R,R*) configuration was assumed, and will be summarized

(8) Kolb, H.; Van Nienwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.

(9) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers: New York, 1986. Sagiv, J. *Tetrahedron* **1977**, *33*, 2303.

(10) The term "couplet" has been introduced in 1971 (Haas, G.; Hulbert, P. B.; Klyne, W.; Prelog, V.; Snatzke, G. *Helv. Chim. Acta* **1971**, *54*, 491). A couplet (*i.e.*, the presence on the CD spectrum of two bands having equal intensity and opposite sign corresponding to a strong UV absorption) derives from the coupling of allowed transitions, *i.e.*, a coupled oscillator system. The coupled oscillator method for the interpretation of CD spectra goes back to the seminal papers of Kuhn (*Trans Faraday Soc.* **1930**, *26*, 293) and Kirkwood (*J. Chem. Phys.* **1937**, *5*, 479). This model has been applied to biopolymers by Moffit (*J. Chem. Phys.* **1956**, *25*, 467), Tinoco (*Adv. Chem. Phys.* **1962**, *4*, 113), and Schellmann *et al.* (*J. Phys. Chem.* **1969**, *73*, 228). The first application in the field of small molecules is due to Mason (*Proc. Chem. Soc.* **1962**, 362) who determined the absolute configuration of the "dimer" alkaloid calycanthine. Applications of this model to structural determinations of natural products can be found in: Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy - Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

(11) Gottarelli, G.; Mason, S. F.; Torre, G. *J. Chem. Soc. B* **1970**, 1349.

(12) Heyn, M. P. *J. Phys. Chem.* **1975**, *79*, 2424.

(13) MMX, Serena Software, P.O. Box 3076, Bloomington, IN 47402.

**Table 1.** UV and CD Absorptions of Compounds **1−10** in Hexane

| compound | ε (λ) | ε (λ) | ε (λ) | ε (λ) | Δε (λ) | Δε (λ) | Δε (λ) | Δε (λ) | Δε (λ) |
|---|---|---|---|---|---|---|---|---|---|
| **1** | | 400 (258) | 10 000 sh (220) | 67 000 (190) | | 0.5 (260) | 20 (221) | 64 (197) | −47 (187) |
| **2** | | (260) | 10 000 sh (220) | 52 000 (189) | | | 15 (221) | 59 (197) | −98 (190) |
| **3** | | (270) | 15 000 (222) | 68 000 (200) | | −0.4 (268) | 28 (234) | 100 (208) | −66 (196) |
| **4** | | 1 000 (260) | 12 500 (221) | 56 000 (194) | | | 23.5 (226) | 56 (196) | −36 (185) |
| **5** | | 1 600 (272) | 17 500 (230) | 68 000 (195) | −0.5 (272) | 28 (232) | −3.6 (217) | 29.5 (200) | −22 (184) |
| **6** | | | 33 000 (255) | 69 000 (202) | | 33.3 (260) | −10.2 (238) | 19 (210) | −32 (192) |
| **7** | 500 sh (310) | 10 800 (275) | 121 000 (230) | 130 100 (217) | 0.1 (317) | −0.4 (284) | −0.35 (272) | 238 (230) | −183 (216) |
| **8** | | 10 500 (283) | 106 200 (223) | | | 8 (280) | −164 (228) | 130 (218) | |
| **9** | | 8 500 (286) | 74 300 (227) | | 18 (298) | −12 (271) | 60 (230) | −257 (225) | 92 (209) |
| **10** | | 5 000 (274) | 87 000 (224) | 48 000 (190) | | | 71 (227) | −16 (210) | −24.5 (191) |
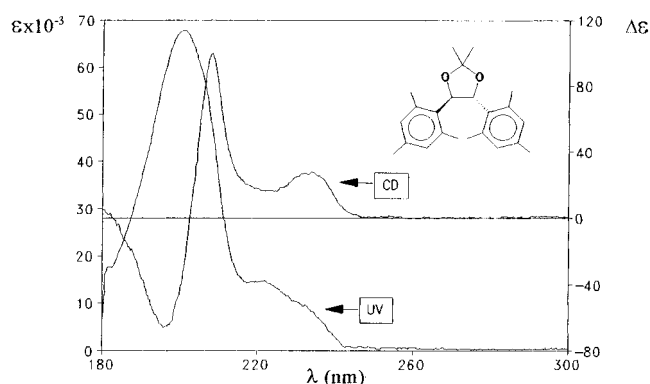


**Figure 1.** Absorption and circular dichroism of (*R,R*)-**3** in hexane.

**Chart 2.** Two Limit Conformation for (*R,R*)-4,5-Diaryl-1,3-dioxolane





**Chart 3**
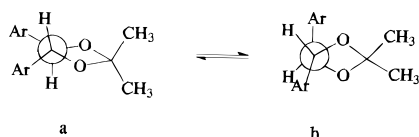
employing the case of **3** as an illustration. In the most stable conformation (Figure 2a), the two aromatic rings assume a quasi-gauche relationship when viewed along the $C_4$–$C_5$ bond, and each phenyl nearly bisects the five-membered ring (Figure 2b). These results are in substantial agreement with the NMR data reported for compound **9**.[14] Further support for the above molecular geometry comes from some CD calculations carried out on compound **3** by means of the coupled oscillators model due to DeVoe.[15] The input parameters are as follows: the molecular structure described above has been employed as input geometry, the 190-nm transition has been described[15] employing a pair of dipoles in the benzene plane (oriented along the Ar–C* direction and perpendicular to it, respectively) carrying $22D^2$ each to reproduce the observed UV intensity. The 230-nm transition has been described by a single dipole polarized along the C*–Ar direction, to which $8D^2$ have been attributed. The calculated absorption and CD spectra show the following
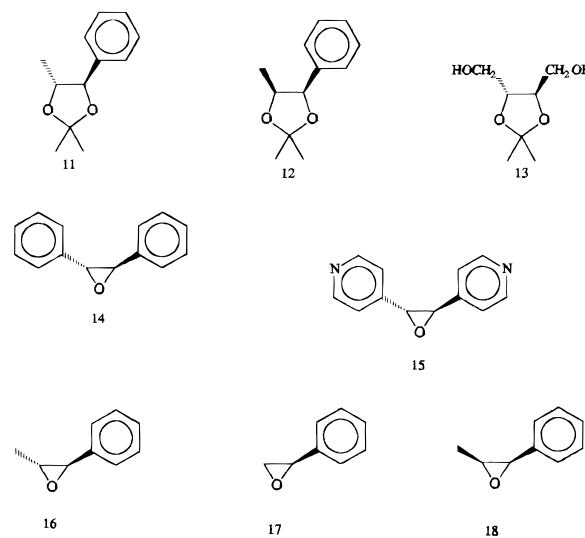
extrema (corresponding experimental values in parentheses):

Absorption: λ 233, ε 16400 (15 000); λ 199, ε 68 200 (68 000)

CD: λ 234, Δε +17 (+14.6); λ 206, Δε +40 (+100); λ 194.5, Δε −60 (−66)

The good agreement between experimental and calculated values strongly supports the prevalence in solution of such a geometry.

As far as compound **5** (Figure 3) is concerned, it contains a different chromophore (a *p*-methoxybenzene system), a benzene ring which is more strongly perturbed than those in the molecules above. The "benzene-like" transitions are well observed at 272 nm (ε = 1600), 230 nm (ε = 17 500), and 195 nm (ε = 68 000). In the CD spectrum, Cotton effects are measured at 270 nm (Δε = −0.4), 232 nm, and 217 nm (Δε = +28 and −4, respectively), which could constitute the extreme of a strongly nonsymmetric positive CD couplet, and the low energy (Δε = + 29.5) of a second positive CD couplet whose negative component reaches Δε = −22 at 184 nm. In summary, the analysis of the CD spectra of derivatives **1−5** shows that while a positive couplet in the region of 200−180 nm is related to the (*R,R*) absolute configuration of the stereogenic centers of these compounds, the intensity values are quite well reproduced using the input geometry provided by the molecular mechanics calculations.

(14) Rosini, C.; Scamuzzi, S.; Uccello-Barretta, G.; Salvadori, P. *J. Org. Chem.* **1994**, *59*, 7395.
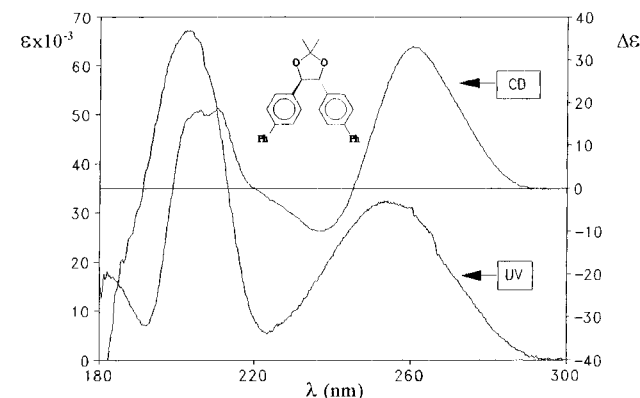
(15) DeVoe, H. *J. Chem. Phys.* **1965**, *43*, 3199. Rosini, C.; Zandomeneghi, M.; Salvadori, P. *Tetrahedron: Asymm.* **1993**, *4*, 545.

$\delta$ (C1'-C4-C5-C1") = +75          $\gamma$ (C5-C4-C1'-C2') = -100
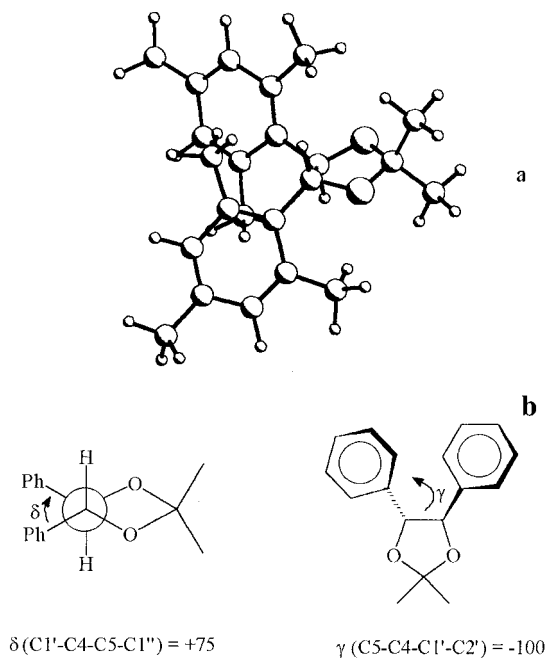
**Figure 2.** Most stable conformation for (*R,R*)-**3** from MMX computation.
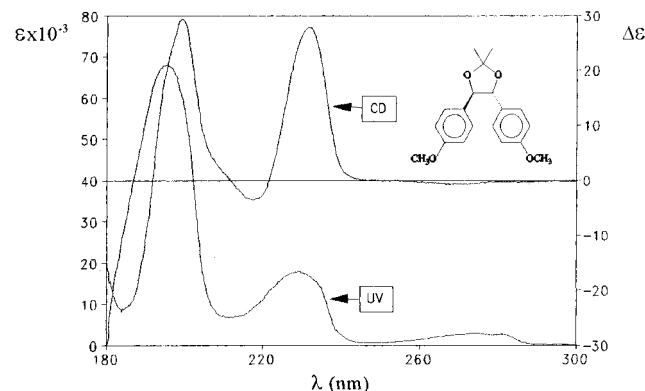


**Figure 3.** Absorption and circular dichroism of (*R,R*)-**5** in hexane.



**Figure 4.** Absorption and circular dichroism of (*R,R*)-**6** in hexane.

The absorption and CD spectra of compound **6** (class b) between 300 and 180 nm are reported in Figure 4. The absorption spectrum is dominated by two intense absorptions at 255 nm ($\epsilon$ = 33 000) and at 202 nm ($\epsilon$ = 69 000). The electronic transitions of the biphenyl chromophore have been studied quite extensively,[16] and allowed transitions having long-

axis polarization have been identified at 252 and 202 nm. In the CD spectrum two positive couplet effects are present: the first one centered at about 245 nm ($\lambda$ = 260, $\Delta\epsilon$ = +33; $\lambda$ = 238, $\Delta\epsilon$ = -10) and the second at 200 nm ($\lambda$ = 210, $\Delta\epsilon$ = 19; $\lambda$ = 192, $\Delta\epsilon$ = -32). For such a molecule, if we assume again (*R,R*) absolute configurations for the two stereogenic centers, we can consider that a structure similar to that reported in Figure 2a is still a correct representation of the overall molecular conformation. In such a geometry the two long-axis directed dipoles of the 250-nm transitions give rise to a positive chirality,[17] and, in fact, a positive couplet is observed in the CD spectrum of **6**, indicating that the sample in our hands has the (*R,R*) absolute configuration. Interestingly, the sign (positive) of the couplet at 200 nm indicates that it is certainly due to a long-axis polarized transition, providing then strong experimental support to the literature assignment. This observation suggests that the analysis of the CD spectrum of a suitable structurally defined "dimer" of a given monomeric chromophore could afford a method for determining the polarization direction of the chromophore itself.[18] Also in this case some coupled oscillator (DeVoe) calculations of the CD spectrum have been carried out. The input parameters (*i.e.*, geometry and spectroscopic data) have been taken as follows: as molecular geometry the structure found by molecular mechanics calculations has been employed placing the oscillators describing the transitions of the biphenyl chromophore in the middle of the $C_{Ar}-C_{Ar}$ bond. The 250-nm transition is due[16] to a set of three excitations having orthogonal polarization (long or short axis), the most intense of which should be the long-axis component; for this reason we felt authorized to describe this absorption band employing a single, long-axis polarized oscillator carrying $22D^2$. Linear dichroism (LD) studies show[16] that the 200-nm absorption band results from two different electronic absorptions at 202 and 208 nm having long- and short-axis polarization and comparable intensity. With this in mind and taking also into account the possibility of free rotation around the $C_{Ar}-C_{Ar}$ bond, which makes impossible the coupling of the short-axis polarized components, we described the 200-nm transition by only one oscillator with a long-axis polarization and carrying half ($22D^2$) of the total dipolar strength allied to this transition. In this way, two strongly nonsymmetric, positive couplets are calculated (+19, -7) and (+13, -27) in full agreement with the experimental data (+33, -10) and (+19, -32).

The absorption and CD spectra of compounds belonging to class c (*i.e.*, **7**, **8**, and **9**) have been described and discussed already,[14] and so they will not be treated here any further. The only aspect that deserves some comment is that the spectra of these compounds look, at a first inspection, very different from each other. Compound **7** shows a positive couplet corresponding to the electrically allowed long-axis polarized $^1B$ transition of the naphthalene chromophore at about 220 nm; compounds **8** and **9** (having the same absolute configuration) show negative couplets in the same spectral region. This behavior can be explained as follows. One can imagine obtaining the structures of **7**, **8**, and **9** starting from the most stable conformation of **3** and creating the second aromatic ring. In such a situation, owing to the different substitution on the naphthalene ring (2,2 *vs* 1,2 *vs* 1,1), the transition dipoles of the $^1B$ transition (which are long-axis oriented within the chromophore) assume a different relative disposition defining a positive chirality in the case of **7** and negative chirality in that of **8** and **9**.

To the class d of these compounds belongs only the derivative **10**, where two different chromophores (phenyl and 2-naphthyl)

(16) Sagiv, J.; Yogev, A.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6861. Rashidi-Ranjbar, P.; Sandström, J. In *4th International Conference on Circular Dichroism*; Bochum (FRG), September 9–13th, 1991, Lectures and Posters, p 152.

(17) See the Harada and Nakanishi, book quoted in ref 10.
(18) Gottarelli, G.; Samorì, B. *Spectrochim. Acta* **1974**, *30A*, 417.
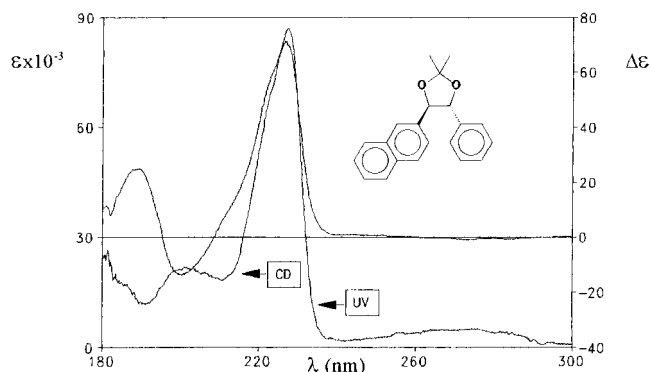
**Figure 5.** Absorption and circular dichroism of (*R,R*)-**10** in hexane.

**Table 2.** Twisting Powers at Room Temperature of Compounds **1**−**18** in the Nematic Solvents[a] MBBA and E7

| | $\beta_M$ (s.d.[b])/$\mu m^{-1}$ | |
|---|---|---|
| | in MBBA | in E7 |
| **1** | −5.4 (2.0) | −17.8 (3.7) |
| **2** | −5.5 (0.1) | −13.7 (0.4) |
| **3** | −59.5 (2.1) | −101 (25) |
| **4** | −18.2 (0.1) | −22.3 (1.7) |
| **5** | −11.0 (0.1) | −26.6 (0.8) |
| **6** | −28.5 (1.6) | −58 (9.9) |
| **7** | −23.1 (3.2) | −36.1 (1.2) |
| **8** | −20.9 (2.9) | −26.2 (4.9) |
| **9** | −48.7 (3.6) | −58.3 (2.3) |
| **10** | −23.6 (0.5) | −37.7 (1.5) |
| **11** | +6.6 (0.1) | +6.8 (0.6) |
| **12** | +0.88 (0.02) | +0.20 (0.02) |
| **13** | +3.1 (0.3) | +4.9 (1.6) |
| **14**[20] | −37 | −32 |
| **15**[19] | −42 | −11 |
| **16**[19] | −8.5 | |
| **17**[19] | −1.2 | |
| **18**[19] | −0.9 | |

[a] MBBA: *N*-(4-methoxybenzylidene)-4-butylaniline (from Reidel-de-Haan); E7: eutectic mixture (from BDH) of 4-cyano-4′-alkylbiphenyl derivatives. [b] Standard deviation.

are linked to the dioxolane ring. The absorption and CD spectra of **10** are reported in Figure 5.

The absorption spectrum of **10** shows the characteristic features of the naphthalene chromophore: a band at 274 nm ($\epsilon$ = 5000) followed by a strong absorption at 224 nm ($\epsilon$ = 87 000), assigned to the $^1B_a$ (short-axis polarized) and to the $^1B_b$ (long-axis polarized) transitions, respectively. They are accompanied by another peak centered at about 190 nm ($\epsilon$ = 48 000). The CD spectrum shows a very weak Cotton effect at 280 nm and a strong band at 227 nm ($\Delta\epsilon$ = +71), *i.e.*, in correspondence with the maximum in the absorption spectrum. Other Cotton effects are observable at 210 nm ($\Delta\epsilon$ = −16) and 191 nm ($\Delta\epsilon$ = −24.5). The strong (+71) CD band which corresponds to the electrically allowed long-axis polarized $^1B_b$ transition of the naphthalene chromophore derives from the coupling of this transition with the Ar−C* polarized component of the phenyl chromophore. If the two stereogenic centers have (*R,R*) configurations, this coupled system gives rise to positive chirality providing a positive couplet; of this couplet we observe the low energy component which coincides with the naphthalene transition at 225 nm.

**Cholesteric Phase Induction: The Twisting Powers.** The twisting powers of the dioxolane derivatives (*R,R*)-**1**−**13** (Charts 1 and 3) measured in the nematic solvents E7 (a biphenyl mixture) and MBBA (a benzylidene aniline derivative) are reported in Table 2 together with some data, taken from the

literature,[19,20] on related compounds with the oxirane ring instead of the dioxolane one; all data refer to the same absolute configuration (*R,R*) of the dopant. A preliminary and purely empirical correlation of configuration for some of these compounds using the liquid crystals technique is reported in ref 2. All diaryldioxolane compounds exhibit negative $\beta$-values in both the solvents investigated. Therefore, there is a strict correlation between the stereochemistry of the dopant and that of the induced cholesteric irrespective of the chromophoric characteristic of the dopant: an (*R,R*) compound induces a (*M*)-cholesteric. The same relationship, (*R,R*) ⇒ (*M*), has been already reported for a few *trans*-diaryloxiranes[19] (see, for example, **14** and **15**); the dimension of the central ring seems not to affect the correlation. This finding supports the idea[3] that in the cholesteric induction phenomenon the solvent "senses" an overall shape-chirality. Analyzing in more detail the twisting power values of the disubstituted dioxolane compounds, it may be noted that the lowest $\beta$ is exhibited by derivatives **1** and **2**, *i.e.*, the compounds with the smallest aryl unit. The increase of the anisometry of the dopant by alkyl or alkoxy *p,p*′-disubstitution leads to higher $\beta$-values (compare **5** and **4** with **1**). A greater effect is induced by a *p,p*′-disubstitution with phenyl rings (see compound **6**). In this case the molecule is not only more elongated, but presents also more planar units. The importance of the presence of planar or quasi-planar units chirally distorted has already been discussed.[3] Furthermore, the presence of a third substituent in the dioxolane ring (see derivative **2**) in a position that does not modify the shape anisotropy of the molecule does not affect the $\beta$-value.

The highest value of $\beta$ is exhibited by derivative **3** in E7; this is one of the highest figures ever reported.[3−5,19−22] The high ability of **3** to twist a nematic phase in comparison to the other related compounds may be connected to the more restricted conformational mobility induced by the *o,o*-disubstitution on each phenyl ring. An effect similar to that induced by the *p*-substitution is observed when the dimension of the aromatic units is increased. In fact, a significant increase of $\beta$-values is observed, in comparison with that of the parent compound **1**, if one or both the phenyl rings are replaced by naphthyl rings (see compounds **7**, **8**, **9**, and **10**). The major differences between the two series of compounds, the dioxolanes and the oxiranes, is the dependence of $\beta$ on the nematic solvent. The dioxolanes **1**−**10** show in E7 $\beta$-values higher than in MBBA; the opposite is shown by the oxiranes **14** and **15**. Later on, we shall discuss a mechanism of induction that may explain this effect. If one or both of the aryl units on the dioxolane ring are substituted by alkyl groups (**11**−**13**), the relationship (*R,R*) → (*M*) is no longer valid and the $\beta$-values are relatively small. The same was reported for the oxirane derivatives **16**−**18**.[19]

**Cholesteric Phase Induction: A Model.** A few years ago, a mechanism was proposed for the transmission of chirality from a dopant to the bulk of the nematic solvent:[4,19] the chiral guest selects chiral conformations of the solvent molecules lying next to it, and these induce chiral conformations in the nearest-neighbor molecules of the solvent and so on. This approach was extensively used to understand the cholesteric induction

(19) Gottarelli, G.; Mariani, P.; Spada, G. P.; Samorì, B.; Forni, A.; Solladié, G.; Hibert, H. *Tetrahedron* **1983**, *39*, 1344.

(20) Gottarelli, G.; Spada, G. P.; Varech, D.; Jacques, J. *Liq. Cryst.* **1986**, *1*, 29−35.

(21) Drake, A. F.; Gottarelli, G.; Spada, G. P. *Chem. Phys. Lett.* **1984**, *110*, 630. Bertocchi, G.; Gottarelli, G.; Prati, R. *Talanta* **1984**, *31*, 138. Gottarelli, G.; Samorì, B.; Fuganti, C.; Grasselli, P. *J. Am. Chem. Soc.* **1981**, *103*, 471. Gottarelli, G.; Hansen, H.-J.; Spada, G. P.; Weber, R. H. *Helv. Chim. Acta* **1987**, *70*, 430. Spada, G. P.; Tampieri, A.; Gottarelli, G.; Moretti, I.; Torre, G. *J. Chem. Soc., Perkin Trans. 2* **1989**, 513.

(22) Gottarelli, G.; Osipov, M. A.; Spada, G. P. *J. Phys. Chem.* **1991**, *95*, 3879.
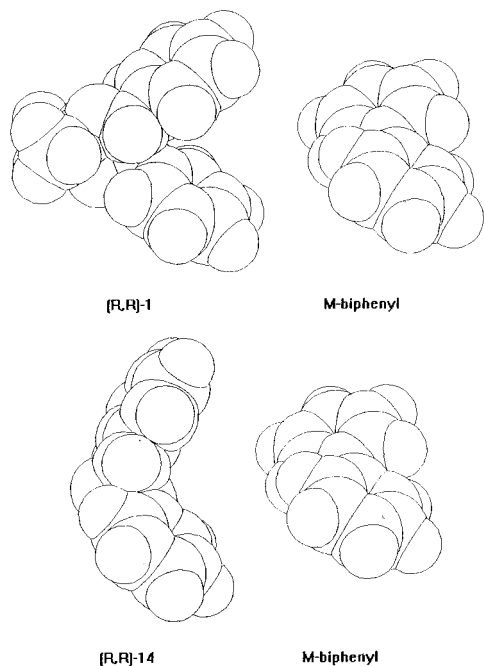
**Figure 6.** Comparison of CPK models of (*R,R*)-**1** (solute) with a biphenyl molecule (nematic solvent) having (*M*)-helicity (top) and of (*R,R*)-**14** with the same biphenyl (bottom). A good fit between solute and solvent results.

caused by biaryl derivatives[4,5] for which relatively high twisting powers are reported. Evidence of the transfer of chirality from solute to solvent was reported also for isotropic solution:[22] it seems reasonable that in the liquid crystalline state, where there is more correlation between molecules, the same transmission is not only operative, but also more efficient. The same mechanism was applied also to induction caused by molecules other than biaryls provided that high twisting powers are observed.[19-22] At the basis of the mechanism there is the assumption of close contact between solute and solvent molecules; this is supported by the fact that an efficient transmission of chirality (high $\beta$s) is observed when solute and solvent are structurally similar, *i.e.*, when both have a biaryl core. Furthermore, the possibility of predicting the configuration of the cholesteric helix is connected to a detailed knowledge of the conformation of the dopant of known configuration. The most stable conformation for dioxolane derivatives resembles, to some extent, that of oxirane analogues; also for these compounds the aromatic rings *quasi*-bisect the aliphatic one. The comparison of these two structures is represented in Figure 6.

Although the dioxolane compound is more globular and less flat, both structures present the two phenyl rings chirally twisted with the same (*M*) handedness: this stereochemical feature may justify the best fitting of these (*R,R*) molecules with the same homochiral (*M*)-biphenyl taken as a model of the solvent molecule. The solvent recognizes the handedness of the dopant and in particular detects the helicity of the twist between the planar (aromatic) moieties. In the present case, all the *trans*-diaryldioxolane molecules induce (*M*)-cholesteric; this means that, following the model, there must be in the dopant a structural unit with a (*M*)-chiral twist. For the conformation derived from the molecular mechanics calculation, this requisite is provided by the (*R,R*) configuration of the diaryl derivatives. This model with an high efficiency transfer of chirality from the dopant to the solvent cannot be operative if one or two aryl groups are replaced by alkyl groups; as a consequence a correlation of configuration is in this case not feasible. In the light of the present model, we can understand why the dioxolane derivatives show higher $\beta$s in E7 while the oxirane compounds do so in
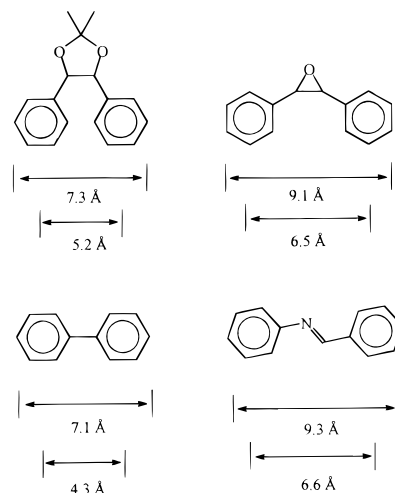


**Figure 7.** A few selected distances as obtained after an MMX computation of two representative dopant compounds and of the core of the two mesogens used.

MBBA. As a consequence of the different size of the heterocyclic ring, the dioxolane compounds are shorter than the oxirane one.

In Figure 7 are reported the distance between the centers of the phenyl rings and the distances between the farthest carbon atoms measured in structures whose conformations were minimized by a MMX routine: for the *trans*-diphenyldioxolane the best fit for the transfer of chirality is with the shorter biphenyl core of E7, while for the *trans*-diphenyloxirane it is with the longer benzylidene aniline core of MBBA.

## Conclusions

The work carried out in this paper has allowed the formulation of an accurate mechanism of cholesteric induction in nematic solvents, by several *trans*-(*R,R*)-4,5-diaryl-1,3-dioxolanes. This has been made possible because, by coupling molecular mechanics calculations and the analysis of CD spectra, a detailed conformational description of the solutes has been achieved. The most stable conformation of the present (*R,R*) derivatives is characterized by a negative (*M*) twist of the aryl rings. It, in turn, determines the prevalence of the *M*-twisted conformation in the biphenyl solvents, causing an overall twist in the bulk of the solvent itself. This investigation has disclosed two main important aspects.

(i) From a spectroscopic point of view, it has been shown that the polarization direction of an electrically allowed transition of a chromophore can be carried out simply by preparing a rigid dimer of the chromophore itself and carefully analyzing the exciton coupling Cotton effects in the CD spectrum.

(ii) The quantitative measurements of the twisting powers shows that dioxolanes like **1**−**10** can induce cholesteric phases having different pitch lengths, depending on the structure of the solute and the nature of the solvent so that the pitch length can be modulated, at least in a certain range. This information, as well as the knowledge of the induction mechanism, will be useful in order to design a dioxolane structure which will induce a cholesteric helix having a selected pitch. This fact may have important consequences from a technological point of view. Work is now in progress along these lines.

## Experimental Section

**General.** Compounds **1**−**3** and **5**−**10** were prepared as previously described.[2] *cis*- and *trans*-1-phenyl-2-methylethane-1,2-diols were prepared following known procedures.[8] 4,4′-Dimethylstilbene was commercially available (Aldrich). NMR spectra were recorded in

$CDCl_3$ on a 200-MHz spectrometer with TMS as reference. Enantiomeric excesses were determined by HPLC analysis carried out with a Jasco Twinkle instrument, using Daicel columns, Chiralcel OJ and Chiralcel OD (eluent: hexane/2-propanol). CD and UV spectra were recorded on a Jasco J-600 spectrometer. Specific rotations, $[\alpha]_D$, are reported in deg/dm at specified temperatures, and the concentration (*c*) is given in grams per 100 mL in the specified solvent.

**(R,R)-(+)-1,2-Di(4-methylphenyl)ethane-1,2-diol.** To a mixture of 7 mL of $H_2O$ and 7 mL of ${}^t$BuOH, in a 50-mL round-bottomed flask, were added 279 mg (0.6 mmol) of dihydroquinidine-9-*O*-(4-chlorobenzoate), 1.19 g (3.6 mmol) of $K_3Fe(CN)_6$, 0.5 g (3.6 mmol) of $K_2CO_3$, and 1.8 mL of $OsO_4$ 0.01 M in $CH_3CN$. After stirring for 15 min at room temperature (rt), the mixture was cooled to 0 °C, 250 mg (1.2 mmol) of (*E*)-4,4′-dimethylstilbene was added, and the mixture was stirred for 24 h at rt. After addition of 1.2 g (9.52 mmol) of $Na_2SO_3$, the resulting mixture was stirred for a further hour, and then the solvents were removed under reduced pressure. Water (5 mL) was added and the mixture was extracted with ether (3 × 20 mL). The organic extracts were dried (NaSO₄), the solvent was removed, and the resulting oil was purified by column chromatography (silica gel: $CH_2Cl_2$/Et₂O 3/1) (yield 82%): mp 111−113 °C [lit.[23] mp 110 °C]; ee 96%; $[\alpha]^{32}_D$ +115 (*c* 0.88, EtOH) [lit.[23] $[\alpha]^{25}_D$ +107 (*c* 1.16, EtOH); ee 92%]; ¹H NMR (200 MHz, $CDCl_3$, δ) 7.05 (s, 8 H); 4.65 (s, 2 H); 2.8 (s, 2 H); 2.3 (s, 6 H).

**(R,R)-(+)-2,2-Dimethyl-3,5-di(4-methylphenyl)dioxolane (4).** To 100 mL of $CHCl_3$, in a 250-mL round-bottomed flask fitted with a Kumagawa extractor, were added 121 mg (0.5 mmol) of (*R,R*)-1,2-di-(4-methylphenyl)ethane-1,2-diol, 0.1 mL of 2,2-dimethoxypropane, and traces of 4-toluensulfonic acid. In the syphon tank, 4 g of molecular sieves (4 Å) was introduced inside a filter pad. After 3 h of reflux, the heat was removed and the reaction mixture was transferred to a separatory funnel and washed subsequentially with 5% aqueous $NaHCO_3$ (2 × 30 mL) and $H_2O$ (2 × 30 mL). The organic layer was

dried ($Na_2SO_4$) overnight and then concentrated to a solid. Ketal **4** was obtained chemically pure after column chromatography (silica gel: $CHCl_3$) (yield 80%); mp 70−73 °C; $[\alpha]^{32}_D$ +92 (*c* 1, $CHCl_3$); ee 96%; ¹H NMR (200 MHz, $CDCl_3$, δ) 7.12 (s, 8H); 4.7 (s, 2H); 2.34 (s, 6H); 1.67 (s, 6H). Anal. Calcd for $C_{19}H_{16}O_2$: C, 80.85; H, 7.80. Found: C, 80.79; H, 7.73.

**(R,R)-2,2,4-Trimethyl-5-phenyldioxolane (11).** Ketal **11**, a colorless oil, was prepared following the same procedure described above (yield, after chromatography, 78%); ee 95%; ¹H NMR (200 MHz, $CDCl_3$, δ) 7.35 (m, 5H); 4.47 (d, 1H, *J* = 8 Hz); 3.87 (dq, 1H, *J* = 8 Hz, *J* = 6 Hz); 1.57 (s, 3H); 1.52 (s, 3H); 1.28 (d, 3H, *J* = 6 Hz). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.38. Found: C, 74.81; H, 8.35.

**(S,R)-2,2,4-Trimethyl-5-phenyldioxolane (12).** Ketal **12**, a colorless oil, was prepared following the same procedure described above (yield, after chromatography, 85%); ee 33%; ¹H NMR (200 MHz, $CDCl_3$, δ) 7.31 (m, 5H); 5.2 (d, 1H, *J* = 7 Hz); 4.55 (m, 1H); 1.65 (s, 3H); 1.46 (s, 3H); 0.8 (d, 3H, *J* = 6 Hz). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.38. Found: 74.97; H, 8.34.

**Induced Cholesteric Measurements.** Cholesteric pitches were measured by means of the "lens" version of the Grandjean−Cano method,[24] 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.[25] A detailed description of the experiments is reported, for example, in ref 26.

(23) Imuta, M.; Ziffer, H. *J. Org. Chem.* **1978**, *43*, 3319.

(24) Heppke, G.; Oestreicher, F. *Z. Naturforsch.* **1977**, *A32*, 899.
(25) Heppke, G.; Oestreicher, F. *Mol. Cryst. Liq. Cryst.* **1978**, *41*, 245.
(26) Gottarelli, G.; Samorì, B.; Stremmenos, C.; Torre, G. *Tetrahedron* **1981**, *37*, 395.