Correlation between Molecular Structure and Helicity of Induced Chiral Nematics in Terms of Short-Range and Electrostatic−Induction Interactions. The Case of Chiral Biphenyls

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Abstract: The helical structure of the chiral nematic phases induced by chiral dopants in nematic solvents provides a macroscopic image of the molecular chirality of the dopant promoted by the orientational order. Chiral biphenyls are challenging systems because their twisting ability shows a strong dependence on the molecular structure, which does not conform to empirical correlation rules. This points out the need for adequate interpretative tools, able to establish a link between molecular properties and macroscopic response. In this paper the twisting ability of chiral biphenyls is reviewed, by reporting examples taken from the literature together with some new experimental results. The microscopic origin of the observed behavior is explained in terms of chirality and anisotropy of short-range and electrostatic−induction interactions. These are described, respectively, by a shape model and a reaction field method, having the common characteristics of a realistic representation of the structure and properties of the chiral dopants in terms of molecular surface, atom charges, and distributed polarizabilities.

Introduction

For a long time it has been known that doping nematic phases with chiral, nonracemic compounds transforms them into chiral nematic nematic phases,[1] characterized by a helical spatial arrangement of the director. Typical values of the helical pitch p are of the order of some micrometers, much larger than the molecular dimensions. For a given dopant concentration, the magnitude and sign of the pitch are strictly related to the chemical structure and, to a lesser extent, to the properties of the nematic solvent, chiral nematics of opposite handedness being induced by enantiomers. Study of the chiral nematic induction has required the definition of the concept of "helical twisting power", i.e., the ability of the dopant to torque a nematic phase.[2,3] This quantity is numerically expressed as

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

where p is the helix pitch, c the dopant molar fraction, and r its enantiomeric excess (the sign of β is taken as positive for a right-handed P-induced chiral nematics).

Investigation of the correlation between molecular and phase chirality is motivated by purposes of applicative and fundamental research. One reason for the interest resides in the possibility of using chiral nematic induction to assess the absolute configuration of chiral solutes, as an alternative to the classical chiroptical techniques, which would be particularly useful for compounds with low optical rotation or when CD spectra are unable to discriminate enantiomers.[4,5] On the other hand, a better knowledge of the molecular mechanism would be valuable for the exploitation of the outstanding optical behavior of chiral nematics, e.g., in the fields of displays or pigments.[6,7] More generally, the investigation of the extreme sensitivity of chiral induction to the molecular structure offers the possibility of getting insight into the chiral interactions and the role of intermolecular forces in condensed phases, which are also at the basis of chiral recognition.[8]

The handedness and pitch of induced chiral nematic phases are determined by the coupling between 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. Some empirical rules have been derived from experimental observations;[4,9] however, their applicability is limited to restricted classes of compounds. A general view would require the understanding of the molecular mechanism at the origin of chiral induction. This can only be

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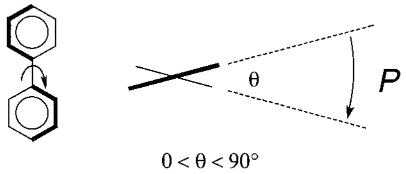

Figure 1. *P*-helicy of the biphenyl core of the compounds investigated.

achieved by using appropriate theoretical tools that are able to establish a link between molecular properties and macroscopic behavior. Approaches of fairly different levels are generally adopted to address this sort of problem. On one hand, single-molecule properties can be described in detail by advanced quantum mechanical methods; however, this information cannot be directly conveyed into condensed phase properties. On the other hand, the statistical mechanics and computer simulation techniques used to describe the behavior of many-body systems are limited to simple idealized objects, thereby neglecting the chemical nature of the systems.[10] Despite the efforts from both the theoretical and the computational points of view, much still has to be done to fill this gap. In this framework falls some recent activity of the Padova group, directed at setting up theoretical methods that are able to account for the behavior of liquid crystals by using a realistic picture of the chemical constituents, in terms of molecular geometry, charge distribution, and polarizabilty. In this paper such methods will be used to explain the chemical structure dependence of the helical twisting power of chiral biphenyls, which appear to be good probes to investigate the relation between molecular and phase chirality for the reasons explained below.

1,1′-Binaphthyls were the subject of much work because of their importance in enantioselective catalysis[11] and in the molecular recognition process. Chiral nematic induction was applied to get information on the structure of the dopant, and it was found that bridged derivatives (in which the twist angle between the two naphthyl units is constrained) induce consistently chiral nematic phases with the same handedness as the helicity along the bond connecting the aryl moieties (*P*-helicity → *P*-chiral nematics).[12−14] Despite the structural similarity, the situation for biphenyl compounds is less simple. In many cases the same trend presented by binaphthyls is observed (*P*-helicity → *P*-chiral nematics),[2,14,15] but the opposite relation (*P*-helicity → *M*-chiral nematics) appears for some derivatives, as we shall report here (see Figure 1 for the definition of *P*-helicity of the biphenyl moiety). Such behavior, which eludes simple rationalizations, is a challenge for theories aimed at a molecular interpretation of macroscopic properties. Actually, the opposite handedness of chiral nematics induced by similar dopants with the same absolute configurations is only a striking manifestation of the general feature that, for a given dopant concentration, the helical pitch depends in a subtle way on the structure of the solute and even small changes in the chemical nature of substituents can affect it. The main characteristics of such a dependence can be explained in terms of steric effects, which change the shape of the dopant,[4] although polarizability has also been considered.[16] In the case of biphenyls, a systematic analysis was undertaken, and a relation with both polarizability and the electron-withdrawing or -donating character of the substituents was suggested.[17] Here we shall review experimental data for a number of dopants with the same (or similar) biphenyl core and various substituents, different in shape and electrostatic properties. Most cases are taken from the literature, while others are reported for the first time.

The ability of biphenyl derivatives with similar structure and the same absolute configuration to induce chiral nematic phases of opposite helicities will be explained here by using a mean field model which takes into account the anisotropy and helicity of the dopant surface:[18] it will be shown that the different shape anisotropy (disk vs rod) and the consequent orientational properties are the main factors in determining the handedness of the chiral nematic phases induced by molecules with similar shape chirality. The theoretical approach is based on the assumption that the orientational distribution of molecules in liquid crystal phases can be related to the amount of molecular surface that is aligned parallel to the mesophase director.[19] The probability of a given orientation increases with the degree of alignment of the surface; this is consistent with the observation that rods and disks tend to orient their symmetry axis parallel and perpendicular, respectively, to the director in calamitic nematics. This model has a phenomenological nature; however, it can be considered as a simple way to account for the short-range interactions whose anisotropy is essentially determined by the molecular shape. As a matter of fact, this model, despite its simplicity, has been proven to be able to explain the molecular structure dependence of the orientational order[19,20] and, more generally, of the mesomorphic behavior of nematic systems,[21] as well as that of macroscopic properties such as the helical pitch of chiral nematics[18,22] and the flexoelectric polarization.[23] Recently, a Monte Carlo technique for the prediction of helical twisting power has been presented, based on an atomistic representation of the chiral dopants modeled as Lennard-Jones particles in a nematic solvent composed of Gay−Berne particles.[24] Results in agreement with experiment were obtained, but at very high computational costs.

The fact that theoretical predictions in agreement with experiment are obtained with the shape model or by simulations using Lennard-Jones and Gay−Berne potentials can be seen as a confirmation of the relevance of short-range interactions for the onset of orientational order in liquid crystals.[25] On the other hand, the contribution of interactions not simply related with the molecular shape, like the electrostatic and induction interactions, cannot be excluded, and it is interesting to explore how they can affect the twisting ability of chiral dopants. To investigate this point, we shall extend here our model for the

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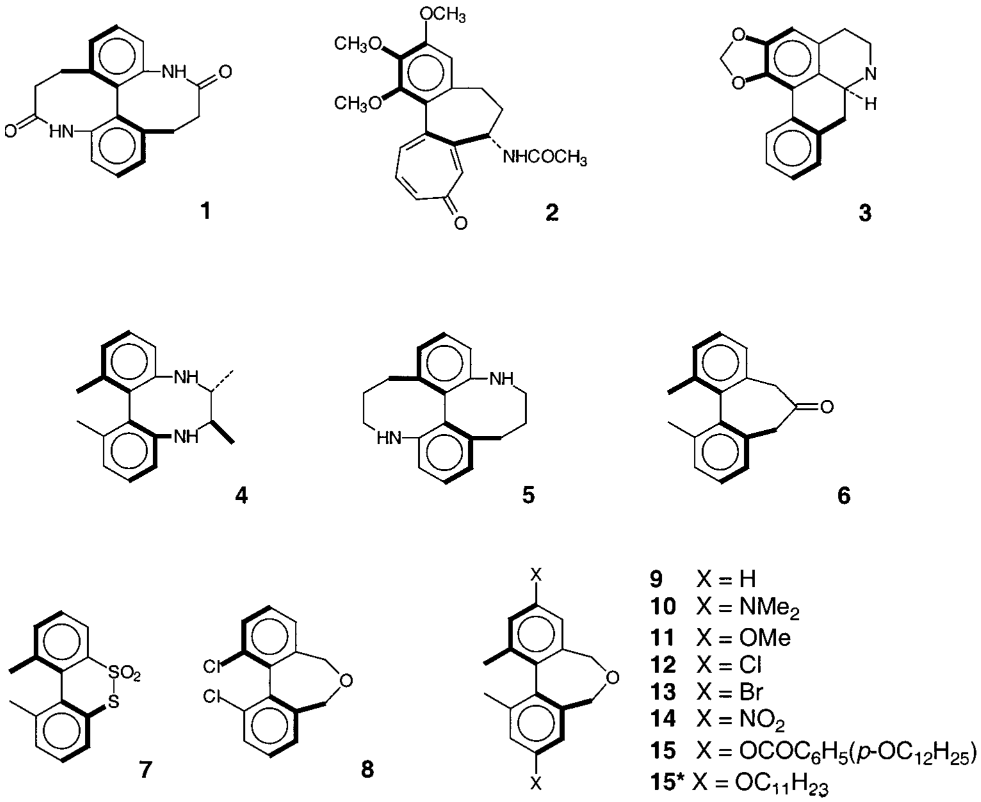
Chart 1. Chemical Structure of Biphenyl Dopants



helical twisting power by including the contribution to orientational order deriving from electrostatic and induction interactions. As far as we know, the present one is the first attempt to model the effect of electrostatic and induction interactions on the twisting power. We have addressed the problem by using a reaction field approximation,[26] whereby electrostatic and induction interactions of the dopant with the solvent molecules are introduced in terms of the coupling between the charge distribution of the former and the electrostatic potential associated with the induced polarization in the surrounding continuum dielectric. In particular, we have used a method which is based on the reformulation of the problem, even in the case of anisotropic dielectrics, in terms of charge density on the molecular surface and gives a detailed picture of the electrostatic and structural properties of the probe molecule.[27−29] Application of our reaction field method to solutes in nematic solvents showed that the contribution of electrostatic interactions is generally non-negligible, even in the case of nonpolar molecules: up to 30% shifts were predicted for the orientational order parameters after introduction of such interactions, with effects increasing with the dielectric anisotropy of the solvent and the magnitude of the atomic charges and polarizability in the solutes.[28,29] In the present paper it will be shown that, by invoking the additional contribution of electrostatic and induction interactions, it is possible to understand the origin of differences in the twisting ability of biphenyl dopants which arise from the chemical nature of the substituents and cannot be explained by the shape model. The magnitude of the effects on the helical twisting power depends on the electrostatic properties of dopants and mesophase, and in some cases dramatic changes are predicted.

Results and Discussion

The common feature of the chiral biphenyls under investigation, **1**−**15** (Chart 1), is the presence of the biphenyl core (or a tropolone-phenyl core in compound **2**) with one (or two) covalent bridge(s), which constrains all compounds to a conformation with *P*-helicity along the biphenyl axis (Figure 1). Despite the common features, the twisting powers are fairly different, spanning from a highly positive value for **1** (+58) to a relatively high negative value for **14** (−20.3), passing through almost negligible values for **8** and **9**. The β values reported in Table 1 are measured at room temperature (in some cases at $T = T_{NI} - 5$ K) in the commercial nematic solvent K15 (4,4′-pentylcyanobiphenyl, $T_{NI} = 308$ K) or at room temperature in E7 (a mixture of cyanobiphenyls and -terphenyls, $T_{NI} = 335$ K) and are in part taken from the literature: data for **3** and **7** are taken from ref 14, data for **1**, **4**, and **5** from ref 15, data for **2** from ref 9, and data for **6** from ref 2; finally, values for **9**, **10**, **12**−**14** were published in refs 17 and 30.

Theoretical Background and Computational Methods. The helical twisting power of a given dopant in a nematic solvent with the twist elastic constant K_{22} and molecular volume v can be calculated as[18]

$$\beta = \frac{N_A \xi}{2\pi K_{22} v} Q \tag{1}$$

where N_A is the Avogadro number, ξ is a temperature-dependent parameter giving the strength of the orienting interactions in

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Table 1. Twist Angles, Principal Values of the Ordering Matrix ***S*** and Corresponding ***Q*** Tensor Components, and Chirality Parameter Q Calculated for the Biphenyl Dopants[a]

compd	θ/deg	S_{xx}	S_{yy}	behavior[b]	x axis direction[c]	Q_{xx}	Q_{yy}	Q/Å^3	β/μm^{-1}
1	+65.8	+0.034	−0.212	*disc*	*ab* plane	+4.8	+22.9	+7.8	+58[d]
2	+59.7	−0.064	−0.308	*rod*	*ab* plane	+11.4	+7.2	+8	+42[e]
3	+18.8	+0.104	−0.332	disc	*ab* plane	−14.1	+16.6	+6.2	+24[e]
4	+64.8	+0.070	−0.224	disc	*b*	+63.4	+5.9	+6.2	+21[d]
5	+62.3	+0.080	−0.268	disc	*b*	+40.6	+5.6	+5.6	+20[d]
6	+57.9	+0.074	−0.230	disc	*a*	−59.1	+23.4	+3.4	+15[g]
7	+46.2	+0.040	−0.246	*disc*	*ab* plane	−41.0	+24.1	+3.4	+5[f]
8	+55.4	+0.016	−0.220	*disc*	*a*	−59.4	+38.8	+4.1	−1.5[h]
9	+54.8	+0.012	−0.220	*disc*	*a*	−58.6	+30.6	+1.2	±0.3[h]
10	+53.8	−0.188	−0.334	rod	*a*	−135.4	+105.7	−4.6	−4.2[i]
11	+52.8	−0.154	−0.308	rod	*a*	−74.7	+45.5	−8.8	−11.4[h]
12	+54.8	−0.126	−0.284	rod	*a*	−70.0	+42.0	−6.8	−17.2[i]
13	+52.1	−0.146	−0.290	rod	*a*	−69.4	+41.5	−8.3	−19.3[i]
14	+55.4	−0.130	−0.306	rod	*a*	−112.7	+84.8	−0.6	−20.3[i]
15									−45[h]
15a*	+51.8	−0.412	−0.438	rod	*a*	−222.5	+169.6	−50.8	
15b*(×2)	+51.9	−0.426	−0.440	rod	*a*	−174.9	+185.3	+13.1	
15c*	+52.0	−0.418	−0.440	rod	*a*	−220.4	+171.6	−47.8	
15*(av)								−27.5	

[a] Calculations have been performed with $U_{\mathrm{mf}} = U_{\mathrm{s}}$. The twisting powers measured in the cyanobiphenyl-type nematics E7 or K15 are also reported. [b] Molecules are classified as rods or disks according to the definition given inthe text; italics is used for molecules close to the boundary between rods and disks. [c] See Figure 2 for the definition of the *a,b,c* directions. For all molecules $y||c$. [d] In E7, from ref 15. [e] In E7, from ref 9.[f] In E7, from ref 14. [g] In K15, from ref 2. [h] In E7, this work. [i] In K15, from refs 17 and 30.

the nematic phase,[31] and Q is the *chirality parameter*, which is related to the average value of short-range chiral interactions in the nematic phase and is conveniently written as

$$Q = -\sqrt{\frac{2}{3}}(Q_{xx}S_{xx} + Q_{yy}S_{yy} + Q_{zz}S_{zz}) \qquad (2)$$

In this equation, (x,y,z) are the principal axes of the ordering tensor ***S*** and the Q_{ii}'s are the corresponding components of the *surface chirality* tensor, a rank two pseudotensor accounting for the chirality of the molecular surface. Its elements are defined as integrals over the molecular surface:

$$Q_{ij} = \sqrt{\frac{3}{8}}\int_S [s_i(\hat{s} \times \vec{r})_j + (\hat{s} \times \vec{r})_i s_j]\, \mathrm{d}\vec{r} \qquad (3)$$

where $\vec{r}$ is a vector giving the position of a point on the molecular surface and $\hat{s}$ the outward-pointing normal in the same point. The diagonal elements Q_{ii}, which obey the relation $\sum_i Q_{ii} = 0$, provide a measure of the helicity of the molecular surface as viewed along the corresponding axes, with positive and negative values corresponding respectively to right- and left-handed helicity.

The Saupe ordering matrix ***S*** describes the degree of alignment of the molecular axes with respect to the mesophase director (laboratory Z axis), and its elements are defined as[32]

$$S_{ij} = \frac{1}{2}\int [3R_{Zi}(\omega)R_{Zj}(\omega) - \delta_{ij}] f(\omega)\, \mathrm{d}\omega \qquad (4)$$

where $R_{Zi}(\omega)$ is the cosine of the angle between the laboratory Z axis and the i molecular axis, ω are the spherical polar angles defining the orientation of the mesophase director in the molecular frame, and $f(\omega)$ is the orientational distribution function

$$f(\omega) = \frac{\exp[-\,U_{\mathrm{mf}}(\omega)/k_{\mathrm{B}}T]}{\int \exp[-U_{\mathrm{mf}}(\omega)/k_{\mathrm{B}}T]\, \mathrm{d}\omega}, \qquad (5)$$

$U_{\mathrm{mf}}(\omega)$ being the mean-field-orienting potential experienced by the molecule in the orientation ω in the liquid crystal phase. The S_{ii}'s sum to zero, $\sum_i S_{ii} = 0$, and each of them can range between $-1/2$ and 1. A highly positive or negative S_{ii} value corresponds to a strong tendency of the ith axis to be aligned parallel to the director or to lie perpendicular to it, respectively. We shall label the principal axes of ***S*** in such a way that $S_{yy}(< 0) < S_{xx} < S_{zz}(> 0)$; i.e., a molecule tends to align the z axis parallel to the local director, while the y axis preferentially lies perpendicular to the director. For the limiting cases of a rod and a disk, the Saupe matrix components[33] are respectively ($S_{xx} = -a/2$, $S_{yy} = -a/2$, $S_{zz} = a$) and ($S_{xx} = a/2$, $S_{yy} = -a$, $S_{zz} = a/2$), with $a > 0$. Therefore, in general we shall speak of rodlike or disklike molecules according to whether the sign of the major components of ***S*** is positive or negative. In the former case the z axis has a strong propensity to align to the director, and the x and y axes have comparable tendencies to stay perpendicular to it. In the latter the x and z axes have comparable propensities to align with the local director, while the y axis preferentially lies perpendicular to it. At the boundary between the two classes of molecules, the principal components of the Saupe matrix are $S_{xx} = 0$, $S_{yy} = -a$, $S_{zz} = a$, corresponding to the maximum biaxiality of order.

It follows from the property of vanishing trace of ***S*** and ***Q*** that only two of their principal components are independent; if we chose the x and y components, eq 2 can be rewritten as

$$Q = -\sqrt{\frac{1}{6}}[(Q_{yy} - Q_{xx})(S_{yy} - S_{xx}) + 3(Q_{yy} + Q_{xx})(S_{yy} + S_{xx})] \qquad (6)$$

From the relations given above between the components of the Saupe matrix it follows that, in the limiting case of a disk, the chirality parameter can be expressed as $Q = -\sqrt{3/2}Q_{yy}S_{yy}$,

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[31] The parameter ξ is related to the parameter ϵ used in some of the quoted references and in particular in ref 18 according to $\xi = k_{\mathrm{B}}T\epsilon$.

[32] Nordio, P. L.; Segre, U. In *The Molecular Physics of Liquid Crystals*; Luckhurst, G. R., Gray, G. W., Eds.; Academic Press: London, 1979; Chapter 16.

i.e., the phase helicity reflects that of the molecular plane, while in the case of a rod the form $Q = -\sqrt{6}(Q_{xx} + Q_{yy})S_{yy}$ is obtained, expressing the proportionality between the helicity of the induced chiral nematic phase and the average molecular helicity perpendicular to the mesophase director (the *xy* plane according to our notation).

Calculation of the orientational distribution function $f(\omega)$, and then of the order parameters, requires the definition of the orientational mean field potential $U_{\mathrm{mf}}(\omega)$. This is written as the sum of two terms: $U_{\mathrm{s}}(\omega)$, a shape contribution accounting for short-range interactions modeled according to the *surface interaction* method,[19] and $U_{\mathrm{rf}}(\omega)$, a reaction field term describing electrostatic−induction interactions:[28]

$$U_{\mathrm{mf}}(\omega) = U_{\mathrm{s}}(\omega) + U_{\mathrm{rf}}(\omega) \tag{7}$$

The two terms can be calculated on the basis of specific properties of each dopant: the shape part depends on the molecular surface, while the reaction field requires a distribution of point charges and polarizabilities within the surface which defines the molecular cavity. In addition, solvent properties as the orienting strength ξ (for the evaluation of the shape contribution) or average dielectric permittivity $\bar{\epsilon}$ and dielectric anisotropy $\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp}$ (for the reaction field calculation) are required.

It has to be pointed out that according to the present approach the electrostatic−induction interactions contribute to the twisting power through their effect on the orientational ordering. This means that only their contribution to the anisotropy of the mean field, which is proportional to the dielectric anisotropy, is considered, while their contribution to the chirality of the mean field, which should depend on the inhomogeneity of the electric permittivity in chiral nematics, is neglected. From the weakness of such inhomogeneity, and in view of the dominant role played by the short-range interactions described by the shape model,[28,29] we can infer that this contribution should be rather small. Anyway, the magnitude of the chiral electrostatic−induction contribution needs to be assessed; this is a challenging task from the methodological point of view, because the generalization of the reaction field method to nonhomogeneous systems requires the development of new theoretical tools, and will be the subject of future investigation.

Calculation are performed according to the following scheme.

(1) The equilibrium molecular structure is obtained. In the present case full geometry optimization at the HF/6-31G* level was performed, as implemented in the Gaussian 98 package.[34]

(2) Given the equilibrium geometry, the molecular surface, required for the calculation of the chirality tensor $\boldsymbol{Q}$ and of the short-range contribution to the orienting potential $U_{\mathrm{s}}(\omega)$, and for the definition of the molecular cavity in the reaction field term $U_{\mathrm{rf}}(\omega)$, is calculated according to the rolling sphere algorithm,[35] as implemented by Olson and co-workers.[36] Such a surface is defined as the contour drawn by a sphere of radius R rolling over a set of van der Waals beads centered at the nuclear position, and constructed as an assembly of triangles. In our calculations, standard van der Waals radii ($r_{\mathrm{C}} = 1.85$ Å, $r_{\mathrm{H}} = 1.0$ Å and 1.2 Å respectively for aromatic and aliphatic hydrogens, $r_{\mathrm{N}} = 1.5$ Å, $r_{\mathrm{O}} = 1.5$ Å, $r_{\mathrm{Cl}} = 1.8$ Å, $r_{\mathrm{Br}} = 1.95$ Å) were used,[37] together with a rolling sphere radius $R = 3$ Å, which is appropriate to mimic the effects of a generic solvent.[20] Calculations have been performed giving the orienting strength parameter ξ in eq 1 the value $0.035k_{\mathrm{B}}T$ Å^{-2}, suitable for cyanobiphenyl nematics at reduced temperatures $T/T_{\mathrm{NI}} \approx 0.9$.[28] A number of triangles $N_{\mathrm{T}} \approx 3000$ was required to get convergence in the evaluation of the mean field potential.

(3) The reaction field contribution $U_{\mathrm{rf}}(\omega)$is calculated from the interaction energy between the electrostatic potential generated by the point charges embedded in the molecular cavity and a charge density on the molecular surface accounting for the solvent polarization. This charge density is obtained by solving a linear system of algebraic equations which correspond to the discretization of the integral equation formulation of the electrostatic problem on the N_{T} triangles approximating the molecular surface. In anisotropic dielectrics, the charge density and then the reaction field energy depend on the molecular orientation ω. The angular dependence of the reaction field contribution is recovered by appropriately sampling the space of molecular orientations. The permanent charge distribution is described in terms of atomic charges; these are calculated, according to the Merz−Kollman−Singh scheme,[38] by fitting the electrostatic potential (in our case calculated at the HF/6-31G* level) on the molecular surface.[34] The polarizability is introduced through a set of interacting atomic dipoles,[39] with the following parametrization: $\alpha_{\mathrm{C}} = 1.508$ Å^3, $\alpha_{\mathrm{H}} = 0.519$ Å^3, $\alpha_{\mathrm{N}} = 1.126$ Å^3, $\alpha_{\mathrm{O}} = 0.947$ Å^3, $\alpha_{\mathrm{Cl}} = 2.387$ Å^3, $\alpha_{\mathrm{Br}} = 3.360$ Å^3, $\alpha_{\mathrm{S}} = 2.926$ Å^3.[40] In our calculations we have assumed an average dielectric constant $\bar{\epsilon} = 10.2$ and a dielectric anisotropy $\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp} = 13.7$, values appropriate for cyanobiphenyl-like nematics as K15 and E7.

(4) The orientational order parameters, eq 4, and then the chirality order parameter, eq 2, are calculated.

It has to be pointed out that no free parameters enter the calculations. For some quantities (e.g., van der Waals radii and atomic polarizabilities) standard values reported in the literature have been assumed, while for others (orienting strength ξ and dielectric permittivity ϵ) we have used values appropriate for the nematic solvents in which the twisting power of the biphenyl derivatives were measured. Some more ambiguity can exist about the radius of the rolling sphere; as discussed in ref 20, values of the order of a few angstroms seem to be the most reasonable to define the molecular surface experienced by common nematic solvents. The choice of the radius may be critical for the prediction of twisting power in the case of solutes with cavities of dimensions comparable with those of the rolling sphere, but this is not the case for the compounds under investigation. As a matter of fact, test calculations performed for some of our derivatives using radii ranging from 2 to 5 Å have shown changes less than 10% in the chirality parameter.

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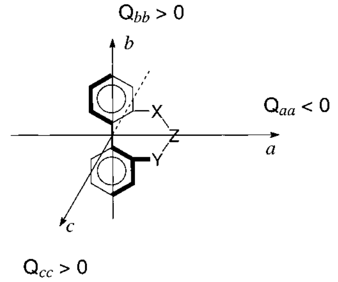

Figure 2. Labeling of molecular axes and corresponding helicities for the biphenyl dopants.

In conclusion, it can be safely stated that, although the predicted twisting powers depend on the values used for the various parameters entering the model, for values contained in physically reasonable ranges effects at most of the order of 10−20% are expected, comparable in sign and magnitude for all the derivatives.

The CPU demand is very different for the various parts of the calculations. Evaluation of shape contribution, orientational order parameters, and chirality parameters, points 2 and 4, can be performed in a few minutes on a PC. The time required by geometry optimization, point 1, depends on the method chosen and can reach some days in the case ab initio methods. Finally, evaluation of the reaction field contribution for a given molecular orientation, point 3, can be performed in times of the order of 5 min on a 500 MHz PC; then, the time required for the full sampling of the orientation space is proportional to the sampling density.

The reader is referred to refs 18, 28, and 29 for an exhaustive presentation of theory and numerical procedure.

The Surface Short-Range Interaction. Calculations with the surface interaction potential $U_s(\omega)$ have been carried out for all the molecules **1**−**15** which possess a homochiral biphenyl unit, and the results are reported in Table 1. In the second column of the table, the twist angles between the phenyl groups, obtained from the ab initio geometry optimizations, are shown. It can be seen that the angles are contained in the range from 46° to 66°, with the larger values in correspondence to the derivatives **1**, **4**, and **5**, with longer bridges connecting the phenyl rings. The only exception is represented by compound **3**, for which a much smaller angle of 18.8° is predicted. In the optimized structures, the nitrogen, oxygen, and carbon atoms of substituents $-NO_2$ in **14**, $-N(CH_3)_2$ in **10**, and $-OCH_3$ in **11** are found to lie in the plane of the attached aromatic ring. Three conformers, corresponding to the three different in-plane arrangements of the methoxy groups, have been taken for derivative **11**; since very similar results have been obtained for all these conformers, only one of them is considered in the table. In the case of molecule **15**, a simplified structure with the substituents $-O(CH_2)_{10}CH_3$ has been considered in the calculations; this is the compound denoted as **15*** in Table 1. Also for this compound three conformers have been considered, corresponding to the different structures with the alkoxy chains, taken in the *all-trans* conformation, on the plane of the attached aromatic ring.

Let us consider now the prediction of the shape model for the orienting behavior of the molecules, described by the ordering matrix $\boldsymbol{S}$. In general, for molecules lacking any symmetry, the direction of the principal axes x,y,z is unknown and can be found only by diagonalization of the ordering matrix $\boldsymbol{S}$. We have found that for most of the molecules under investigation, such axes are approximately parallel to the three axes a, b, and c in Figure 2. In all cases y corresponds to the c axis; this means that the orientations with the director on the "mean molecular plane" are favored. In contrast, z, the axis preferentially aligned parallel to the local director, can correspond to the a or b axis, depending on the molecular structure. In Table 1 we have also indicated the directions of the x axis for the various molecules. Only the two independent order parameters S_{zz} and S_{yy} are reported in the table; S_{zz} can be obtained from the latter as $S_{zz} = -S_{xx} - S_{yy}$. We can see that, according to the definition given above, the compound **2** and the derivatives **10**−**15**, which bear substituents in the 4,4′ position, have a rodlike behavior. In contrast, compounds **1** and **3**−**9** can be classified as disklike. Such labels are used in Table 1. This classification will be useful to rationalize the different twisting ability of the molecules; however, it should be kept in mind that this is an oversimplification of the real behavior, which in all cases is characterized by a significant biaxiality of ordering. This holds in particular for the derivatives **1**, **2**, and **7**−**9**, which lie very close to the boundary between rods and disks, with no net features in one direction or the other.

According to our model, the chirality of the solute−solvent interactions is quantified by the helicity tensor **Q**, eq 3. In Table 1 we have reported the elements Q_{xx}, Q_{yy}, measuring the helicity of the molecular surface along the x and y principal axes of the ordering matrix $\boldsymbol{S}$, which appear in the expression of the chirality parameter Q, eq 6. The element Q_{zz} is not reported, but it can be obtained as $Q_{zz} = -Q_{yy} - Q_{xx}$. The off-diagonal elements, which do not enter eq 3, are not shown in the table; however, we can mention that for most of these biphenyl derivatives they are close to zero, which means that the principal axes of the **Q** tensor are close to the principal axes of the $\boldsymbol{S}$ matrix. It appears from Table 1 that Q_{yy}, the helicity perpendicular to the "molecular plane", is positive for all derivatives, while Q_{xx} can be negative or positive according to the direction of the x axis (Q_{xx} is positive or negative when x is parallel to the b or a axis, respectively). It can be seen that the sign of the helicity along a given molecular axis corresponds to what can be expected from the molecular geometry (opposite values would be predicted for the *M* enantiomers). For example, a positive value is predicted for the helicity along the 1,1′-axis, in agreement with the rule adopted to assign the *P* label to the enantiomers considered in the present work.

The correlation between orientational behavior and sign of the helical twisting power clearly appears from Table 1: positive and negative twisting powers correspond to disklike and rodlike molecules, respectively. Thus, we can infer that the different shape behavior (disk vs rod) and the consequent orientational properties (S_{ii}) must be the main factors in determining the sign of the chirality parameters Q (and hence of β's) for these molecules with roughly similar shape chirality (Q_{ii}). The different orientational behavior corresponds to a different averaging of the similar chiral interactions of the biphenyl systems, owing to the differences in the anisotropy of the interactions. The limiting cases of rods and disks considered above help us understand the mechanism of chiral induction for biphenyl dopants. The structures with a more disklike shape have a pronounced tendency to align the "mean molecular plane" (*ab* plane in Figure 2) perpendicular to the helix axis, so producing helical superstructures with the same helicity of this plane. Since in our case such a helicity is positive, right-handed chiral nematics are produced. In contrast, for biphenyls with more elongated structures, the two axes perpendicular to the long molecular axis (the c and a axes in Figure 2) have comparable propensity to align with the axis of the macroscopic helix, so that the molecular helicities along these axes will affect the pitch in similar ways. In particular, since the two molecular helicities are opposite in sign, with the former positive and smaller in magnitude than the latter, left-handed chiral nematics are induced. It is worth reminding that the structure of bridged-1,1′-binaphthyls corresponds (usually) to a disklike behavior; this is the reason the correspondence *P*-helicity → *P*-chiral nematics is (usually) observed for such systems.

We have seen that, on the basis of the theoretical results, it is possible to give a simple and clear explanation for the apparently contradictory behavior of biphenyl dopants. We can now look in more detail at the numerical predictions. For such a comparison between theory and experiment, we should calculate the twisting power β which, according to eq 1, is related to Q by a factor which depends on the nematic solvent and the temperature. The reported data are taken from different experimental determinations at room (in general not constant) temperature and in solvents which, although similar in nature, are not exactly the same and have different nematic–isotropic transition temperatures; therefore, the proportionality factor is expected to be slightly different from case to case. For these reasons, in considering the theoretical predictions, we shall refer only to the Q values, recalling that for the solvents under investigation the proportionality factor should be of the order of unity (see eq 1). Another important point which should be kept in mind when comparing theoretical and experimental results is that the Q values are determined by the molecular geometry; therefore, the quality of the predictions depends on how the available structures are close to the real ones in the nematic solvents. For most of the systems under investigation this should not be a big problem, because the geometries of the bridged biphenyl cores are expected to be essentially determined by intramolecular constraints. The only derivatives to be taken with more care are those characterized by some flexibility, for which only one, or at most a few conformers have been taken, corresponding to the potential energy minima in a vacuum. From Table 1 we can see that the Q values scale rather well with the measured twisting powers, with a scale factor of about 3–4. The only significant discrepancies from this general trend are observed for derivatives **7**–**9** in addition to **10**, **11**, and **14**. The former set of compounds lie somehow at the border between the two classes of disks and rods and have very small twisting abilities; the calculated Q values result from the compensation of comparable contributions of opposite signs and can be strongly affected by small changes in the order parameters. Therefore, even relatively small inaccuracies in the calculated order parameters, which can derive from uncertainties in the molecular geometry or from the intrinsic limits of the method, are expected to produce fairly large errors in the predicted twisting powers. More surprising is the low quality of the predictions for derivatives **10**, **11**, and **14**, which have a similar structure with net rod orientational behavior. A possible explanation is the quite different electrostatic character of the substituents, which of course cannot be taken into account by the shape model. There is no simple way to predict, even at a qualitative level, how these interactions can influence the orientational ordering and then the twisting ability of chiral dopants; therefore, an appropriate theoretical methodology to account for the electrostatic interactions has to be used. This point will be considered in the next section.

Some further attention should be given to compound **15***, for which the role of flexibility cannot be neglected, even at the lowest level of approximation. We can see that the presence and the geometry of the two tails have strong effects on both the orientational behavior and the chirality: as a consequence of the definitely elongated shape, the orientational behavior of an almost perfect rod is predicted for the three conformers, with very high order parameters and large helicities. Similar and extremely high negative twisting powers are predicted for the two conformers having both substituents on the same side with respect to the 1,1′-bond (**15a*** and **15c***, C_2 symmetric), while a positive Q value, lower in magnitude, is calculated for the conformers with the two substituents on opposite sides (**15b***). This example demonstrates the importance of a careful conformational analysis to obtain reliable predictions for systems with massive flexibility. By averaging over all conformers, a fairly large negative Q value is obtained. When comparing with the experimental result, it should be considered that calculations have been performed for a structure which does not exactly correspond to molecule **15**, but only bears the same characteristic of two long substituents in the 4,4′-position. Moreover, the flexibility of the alkyl chains has been neglected in the calculations, and this leads to an overestimation of its twisting ability. Despite all this, a general agreement with the experimental behavior can be observed; from a comparison with the other biphenyl derivatives, and in particular with the homologous molecule **11**, a remarkable enhancement of the twisting ability appears as a consequence of the introduction of the longer substituents.

The Role of the Electrostatic–Induction Interactions. For molecules **6**–**14**, which are fairly similar in structure, we have performed calculations with the more general orienting potential eq 7 which includes, in addition to the shape contribution, the reaction field term accounting for electrostatic and induction interactions. In the framework of the reaction field approximation, the anisotropy of electrostatic interactions, and thus the effects of these interactions on orientational ordering, depend on the charge distribution and shape of the probe molecule, while the electrostatic properties of the solvent molecules do not enter in a direct way, but only through the dielectric anisotropy $\Delta\epsilon$ of the medium.

The ability of a molecule to establish strong electrostatic interactions with the surroundings is related to the magnitude of the local charges and the extent to which they are exposed to the solvent. The atomic charges obtained from the ab initio calculations are different for the molecules under investigation; however, a common pattern can be found, characterized by relatively large charges on carbons, and smaller ones on hydrogens, which however can have significant effects since these atoms are smaller and more exposed to the solvent, and a large negative charge, also well exposed to the solvent, on the bridge oxygen. In the case of the dinitro derivative **14**, additional strong charges are located on the atoms of the nitro groups. The electrostatic features of the various derivatives cannot be discussed in detail; only the main differences will be illustrated here and in the following by referring to the derivatives **10** and **14**, taken as representative of behaviors which fall at opposite ends. The two images on the left side of Figure 3 show the electrostatic potential generated by the atomic charges on the molecular surface of these derivatives. Red and blue correspond to negative and positive potentials, while whitish colors indicate vanishing values of the potential. Thus, strongly colored zones correspond to regions that are able to establish strong electrostatic interactions. While for the diamino derivative **10** such regions are localized in the neighborhood of the bridge oxygen atom, in the case of the dinitro compound **14** significant effects appear also in correspondence with the nitro substituents.

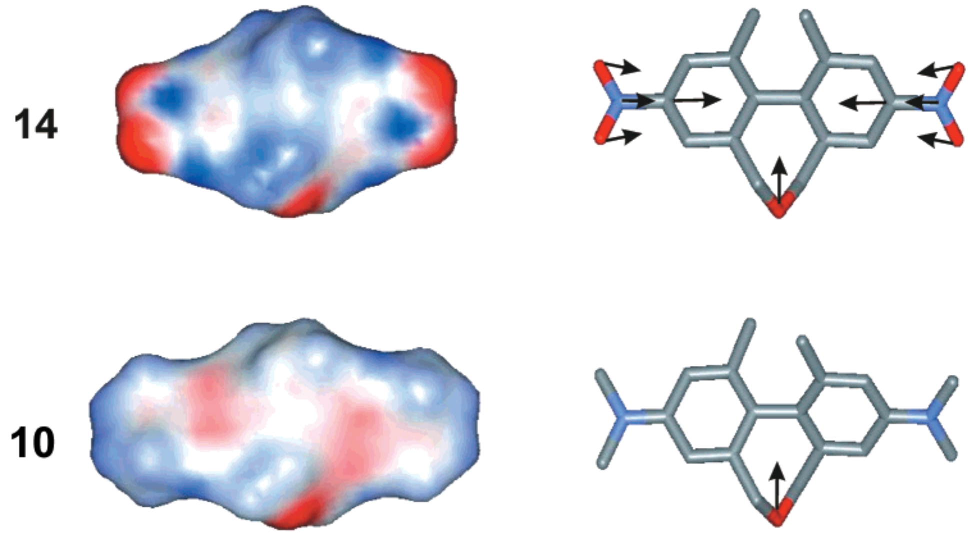

Figure 3. Difference in the electrostatic properties of derivatives **10** and **14**. Left: electrostatic potential generated by the permanent charges on the molecular surface; red and blue represent negative and positive values of the electrostatic potential, respectively. The representation was obtained with WebLabViewerPro 3.7 (2000, by Molecular Simulation), using the ab initio charges. Right: atom dipoles induced by the reaction field; only dipole moments larger than 0.2 D are shown, with arrows pointing from the negative to the positive charge.

Table 2. Molecular Polarizabilities (Å^3) Calculated for Molecules **6**−**14**[a]

	α_{zz}	α_{xx}	α_{yy}	$\bar{\alpha}$
6	31.7	28.8	19.9	26.8
7	33.0	30.1	19.8	27.6
8	31.0	27.2	19.7	26.0
9	31.2	26.5	19.1	25.6
10	50.3	35.1	26.4	37.3
11	43.5	31.0	22.7	32.4
12	41.8	28.8	21.6	30.7
13	46.4	30.1	23.0	33.2
14	40.8	29.9	21.7	30.8
biphenyl	29.1[b]	20.3[b]	12.9[b]	20.8[b]
	24.7[c]	20.3[c]	13.8[c]	19.6[c]

[a] The diagonal elements α_{ii} (with the axes labeled as in Table 1, and approximately corresponding to the principal axis of the α tensor) and average value $\bar{\alpha}$ are reported. For the sake of comparison, experimental values for biphenyl are also reported. [b] Reference 41. [c] Reference 42.

Our model also takes into account induction interactions, derived from the fact that the charge distribution in a molecule is modified by the electrostatic fields determined by the presence of surrounding molecules (in our language, the charge distribution is modified by the reaction field itself). According to the Thole model we have adopted, the distortion of the electronic cloud of a molecule in the presence of an electric field is described in terms of induced mutually interacting dipoles located at the atomic positions. Table 2 reports the molecular polarizabilities obtained in this way. When compared with the experimental values of the polarizability tensor for biphenyls, also reported in the table, and with the average polarizabilities derived from refractive indexes of substituted benzene,[17] the theoretical results appear to provide an acceptable representation of the response of the electronic cloud to a uniform field for the systems under investigation. More pertinent information about the response to the nonuniform field generated by the surrounding molecules can be obtained from the analysis of the dipoles induced by the reaction field at the different atomic positions. These are shown in the two images on the right-hand side of Figure 3 for molecules **10** and **14**. Again, significant differences appear between the two molecules, with strong induced dipoles limited to the neighborhood of the bridge oxygen in the case of **10**, and extended to the nitro substituents for **14**.

As a consequence of the different electrostatic and induction behavior, different orientations are stabilized when the dopants are dissolved in a solvent with positive dielectric anisotropy. From a qualitative point of view, we can expect that such interactions will be stronger for the orientations which allow regions of the molecular surface with large gradients in the electrostatic potential to lie in the direction of higher permittivity (i.e., parallel to the director in nematics with $\Delta\epsilon > 0$). The specific effects for a given derivative depend on its particular charge distribution; however, a general trend, also observed for planar aromatic solutes,[28,29] is that the reaction field interactions decrease the tendency of the "molecular plane" to lie perpendicular to the local director. This leads to a general decrease of the orientational order produced by short-range (surface) interactions, as appears from the order parameters S_{ii} reported in Table 3. The only striking exception is represented by the dinitro derivative **14**, for which the reaction field interactions favor alignment of the 1,1′-axis (*b* axis) with the local director, thereby enhancing the effect of the short-range surface interaction.

For the molecules under investigation, the reaction field contribution does not modify (or slightly modifies in the case of derivative **7**) the principal axes of ordering; therefore, the Q_{ii} values, being practically the same as those in Table 1, are not reported in Table 3. It is interesting to see that, even though the change in order parameters never exceeds 25%, dramatic effects on the Q value can result: for **14** it increases by an order of magnitude, and for **10** a 100% change is predicted. In all cases it can be seen that the magnitude and sign of the changes in Q due to the introduction of the reaction field contribution in the orienting potential are such that agreement with the experimental behavior is improved. Namely, the trend of the Q values reported in Table 3 is in close correspondence with that of the measured twisting powers. The only derivatives for which significant discrepancies still appear are molecules **7** and **8**, and the reasons have been mentioned in the previous section; anyway, the small magnitude of the predicted Q values, which tend to decrease by virtue of the electrostatic−induction

Table 3. Principal Values of the Ordering Matrix ***S*** and Chirality Parameter *Q* Calculated for the Biphenyl Dopants[a]

compd	S_{xx}	S_{yy}	behavior[b]	*x* axis direction[b]	Q/Å^3 [a]	$\beta/\mu\text{m}^{-1}$ [b]
6	+0.079	−0.225	disc	*a*	+3.8	+15
	(+0.074)	(−0.230)	disc	*a*	(+3.4)	
7	+0.056	−0.246	*disc*	*ab* plane	+3.1	+5
	(+0.040)	(−0.246)	*disc*	*ab* plane	(+3.4)	
8	−0.014	−0.224	*rod*	*a*	+2.4	−1.5
	(+0.016)	(−0.220)	*disc*	*a*	(+4.1)	
9	−0.002	−0.204	*rod*	*a*	+0.2	±0.3
	(+0.012)	(−0.220)	*disc*	*a*	(+1.2)	
10	−0.162	−0.314	rod	*a*	−2.4	−4.2
	(−0.188)	(−0.334)	rod	*a*	(−4.6)	
11	−0.104	−0.292	rod	*a*	−5.7	−11.4
	(−0.154)	(−0.308)	rod	*a*	(−8.8)	
12	−0.108	−0.270	rod	*a*	−5.5	−17.2
	(−0.126)	(−0.284)	rod	*a*	(−6.8)	
13	−0.124	−0.274	rod	*a*	−6.4	−19.3
	(−0.146)	(−0.290)	rod	*a*	(−8.3)	
14	−0.184	−0.331	rod	*a*	−5.9	−20.3
	(−0.130)	(−0.306)	rod	*a*	(−0.6)	

[a] Calculations have been performed with $U_{\text{mf}} = U_{\text{s}} + U_{\text{rf}}$. For the sake of comparison the twisting powers and the results obtained in the absence of electrostatic and induction interactions, i.e., $U_{\text{mf}} = U_{\text{s}}$ (between brackets), are also reported. [b] See footnotes of Table 1.

interactions, corresponds to the experimental findings for these molecules at the border between rods and disks.

The electrostatic−induction calculations reported have been carried out for nematics with high dielectric anisotropy, as are the solvents in which the twisting powers reported in Table 1 were measured. It could be shown that the electrostatic−induction effects on the mean field potential eq 7 for a given molecule are roughly proportional to the ratio $\Delta\epsilon/\bar{\epsilon}$; this means that the changes in order parameters are expected to be monotonic function of the dielectric anisotropy and to change their sign with it. Thus, we expect that the twisting powers measured in solvents with lower values of $\Delta\epsilon/\bar{\epsilon}$ should be closer to those predicted only on the basis of the surface interaction model.

Conclusion

In this paper we have presented an overview of the twisting ability of bridged biphenyl dopants, which constitute an interesting case because of their ability to induce chiral nematics with different pitch and handedness as a consequence of relatively small structural changes in the homochiral biphenyl unit. We have shown that the main features of the experimental behavior, and in particular the induction of chiral nematics with opposite handedness by dopants with the same absolute configuration and only small structural differences, can be explained by a shape model accounting for the chirality and the anisotropy of the short-range intermolecular interactions in terms of anisometry and helicity of the molecular surface. The results reported confirm the ability of such a theoretical approach to describe the coupling between chirality and orientational order, which had already been proven for various classes of chiral dopants.[5,22] The method has the valuable feature of providing reliable predictions with a minimal computational demand. Therefore, it can be used also for complex chiral systems, of arbitrary dimension and with flexible groups, in which case predictions of twisting power may require an accurate sampling of the conformational space.

We have herein presented an extension of the theoretical method, by introducing the further contribution from electrostatic and induction interactions to orientational order of the chiral dopants. We have seen that this contribution may have a significant effect on the presence of substituents with a strong electron-donating or -withdrawing character and significant polarizability. Analogous conclusions about the general relevance of short-range surface forces, together with a strong dependence of the magnitude of electrostatic and induction interactions on the chemical structure of the molecules, were reached not only in the analysis of the molecular mechanism at the origin of liquid crystal ordering,[28,29,43,44] but also in the study of chiral recognition.[8]

A clear and fairly simple picture emerges from the microscopic analysis of chiral induction presented here, which allows the rationalization of the apparently complex experimental behavior of chiral biphenyls. It can be summarized in the following way. The chirality of bridged *P*-biphenyls with different substituents, as measured by the chirality tensor eq 3, is in general characterized by positive helicities perpendicular to the approximate molecular plane and along the 1,1′-axis, and a negative helicity along the C_2 (or quasi-C_2 axis). In the presence of substituents in the 6,6′-positions, the orientational behavior of the dopants can be assimilated to that of disks, which tend to keep the molecular plane on the mesophase director. When substituents are introduced in the 4,4′-positions, the dopant shape becomes more elongated, and a rodlike behavior is predicted, characterized by the tendency to align the long molecular axis with the director. The different orientational behavior corresponds to a different averaging of the chiral interactions felt by the solvent. The dopant helicity experienced perpendicularly to the director, where the macroscopic helix develops, is the one (positive) of the molecular plane in the former case, while in the latter situation it is the average of the molecular helicities perpendicular to the elongation axis (one smaller and positive, the other larger and negative). Thus, chiral nematics of opposite handedness are induced. The theoretical analysis provides a simple rule for the correlation between chemical structure and twisting power of biaryl dopants: the rule *P*-helicity → *P*-chiral nematics is expected to hold only for disklike systems (binaphthyls and discoid biphenyls) and should be substituted by *P*-helicity → *M*-chiral nematics in the case of derivatives elongated in the direction of the aryl−aryl bond.

Electrostatic and induction interactions introduce an additional alignment mechanism, dependent upon the molecular shape and charge distribution, which modulates the effects of the short-range interactions, according to the nature of the substituents. The relevance of the reaction field contribution is expected to depend on the charge distribution and polarizability of the probe molecule and on the dielectric permittivity of the solvent (with no contribution for vanishing dielectric anisotropy). In the case of aromatic solutes in nematic solvents with $\bar{\epsilon} \approx 10$ and $\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp} \approx 10$, typical values for cyanobiphenyl-like nematics, effects up to 30% on the order parameters were predicted. In the case of the twisting power it appears that, although electrostatic and induction interactions only enter through ordering, the final effect can be much more pronounced than that on the order parameters.

We can conclude that in the present work the correlation between molecular structure and twisting ability of biphenyl dopants has been clarified. The theoretical method presented here, based on a realistic representation of the molecular structure and properties, appears to be able to give valuable insight into the nature of the chiral interaction and the role of

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intermolecular forces in determining orientational order and twisting power.

Experimental Section

Helical twisting powers have been measured at room temperature in the commercial nematic solvent E7 (from Merck) using the lens version of the Grandjean−Cano technique.[45,46]

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