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A Correlation between the Absolute Configuration of Alkyl Aryl Sulfoxides and Their Helical Twisting Powers in Nematic Liquid Crystals

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In this paper, for the first time, a systematic experimental and theoretical analysis of the cholesteric induction due to solutes whose chirality is originated only by a single stereogenic center has been carried out. The twisting power β of a series of alkyl aryl sulfoxides has been determined in several nematic solvents. The sign of β, which reflects the handedness of the induced helical arrangement of the solvent molecules, correlates with the configuration of the stereogenic sulfur in the nematic solvents E7, Phase 1083, and ZLI 2359: (*S*)-configurated dopants induce (*M*)-chiral nematics. (*S*)-Configurated cyclic sulfoxides, which are forced to adopt a different conformation with respect to the parent acyclic compounds, induce, instead, right-handed chiral nematics. The experimental data have been interpreted in the light of the surface chirality model, which allows the calculation of β in terms of the molecular properties of the dopant, namely, the anisotropy and helicity of its molecular surface. The calculations reliably reproduce the behavior experimentally observed. The more flexible, open-chain compounds investigated induce chiral nematics of opposite handedness in MBBA and Phase 1053: temperature-dependent experiments point out the importance of the conformation in determining the effective sign of β. The results have been discussed in terms of different conformation populations in these latter solvents with respect to E7, Phase 1083, and ZLI 2359.

Introduction

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

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

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

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

The handedness and pitch of induced chiral nematic phases are determined by the coupling of the chirality and orientational behavior of the dopants; therefore, the relation between the configuration of the dopant and the sense of the phase is neither simple nor obvious.[7] Some empirical rules correlating the stereochemistry of the dopant to the handedness of the phase have been derived

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from experimental observations;[4,8] however, their applicability is limited to restricted classes of compounds. A general use of the technique would require an understanding of the molecular mechanism at the origin of the chiral induction.

The phenomenon of chiral induction originates from the torque exerted by the chiral probe on the local nematic director, which is transmitted at a distance by virtue of the elastic properties of the liquid crystalline phase. A quantitative relation between β and the molecular structure of the chiral dopant can be theoretically derived by the surface chirality model, which accounts for the short-range solute−solvent interactions modulated by the solute molecular shape.[9,10] The model rests on the assumption that the anisotropy and chirality of such interactions, which determine the twisting ability of the dopant, can be parametrized on the basis of the anisometry and helicity of the molecular surface. The theoretical model has been presented in detail elsewhere[9,10] and only some aspects are reviewed here. The value of β of a given dopant in a nematic solvent can be calculated by eq 2

$$\beta = (N_A \xi / 2\pi K_{22} \nu_m) Q \qquad (2)$$

where N_A is Avogadro's number, ξ, K_{22}, and ν_m are the orienting strength, the twist elastic constant, and the molar volume of the solution, respectively, and Q is the chirality parameter. This depends on the coupling of the chirality and orientational behavior of the dopant. In fact, the chirality parameter Q can be expressed in terms of the ordering (S) and helicity (Q) tensors:

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

The ordering tensor, whose elements S_{ii} give the degree of alignment to the local director of the correspondent *i*-molecular axes, is in turn obtained from a molecular tensor **T**. The **Q** and **T** tensors are calculated by exploring the molecular surface by unit normal vectors; the components T_{ii} and Q_{ii} quantify respectively the anisometry and the helicity of the molecular surface, as viewed along the *i*-axis. The dopant is modeled as an assembly of van der Waals spheres centered at the atomic position; the molecular surface is then defined as the envelope drawn by a sphere rolling over the assembly.[11] Given the molecular structure, calculations can be performed on a desktop computer in a few seconds.

With the help of these theoretical tools,[12] the absolute configuration of different classes of compounds has been assessed from the helical twisting powers measured in nematic phases: helicenes,[13] biphenyl,[14] and binaphthyl derivatives.[15]

To date, this type of treatment has never been applied to compounds displaying simple central chirality (i.e., where the chirality is determined by the presence of a stereogenic center and it is not an overall molecular feature).[16]. We thus decided to employ the analysis of induced chiral nematic mesophases to assess the absolute configuration of chiral alkyl aryl sulfoxides, a class of compounds of great relevance in organic chemistry.[17] Recently, electronic circular dichroism (ECD) spectroscopy has been used to assign the absolute configuration of alkyl aryl sulfoxides by means of a CD spectrum analysis based on the coupled-oscillator mechanism.[18] However, this approach is limited to those compounds where the interacting chromophores (i.e., the SO and the aromatic moiety) are not exchanging electrons. Vibrational circular dichroism (VCD) has also been used for this purpose, demonstrating that this technique could afford a more general approach.[19−21] However, this method is still of limited use nowadays, because the required instrumentation is not widely available yet and the theoretical analysis needed for the spectra interpretation is still difficult to manage (at least for the synthetic organic chemist).

In this paper, we illustrate the use of the nematic doping technique to determine the absolute stereochemistry of a series of alkyl aryl sulfoxides. This is a direct (applicable, without reference to other chiral molecules and not requiring single crystals), rapid method, requiring only simple instrumentation (an optical microscope and a basic computing facility).

Results and Discussion

Acyclic sulfoxides **1**−**17** and cyclic derivatives **18** and **19** (Chart 1) were prepared in an optically active form

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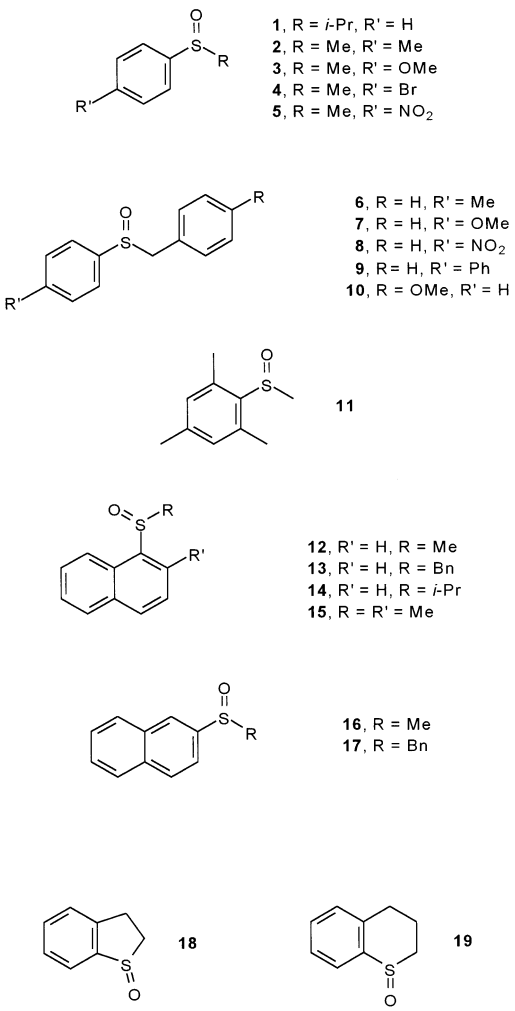
CHART 1



through a stereoselective oxidation of the corresponding prochiral sulfides.[22,23] The absolute configuration was assigned by comparison of $[\alpha]_D$ in the case of the known compounds[24] **1**−**8**, **11**−**13**, and **15**−**19**, and from comparison of the CD spectra with those of similar compounds of known configuration for the remaining derivatives **9**, **10**, and **14**.

The β values of compounds (*S*)-**1**−**17** measured in nematic solvents E7, Phase 1083, ZLI 2359, MBBA, and Phase 1052 (Chart 2) are reported in Table 1.

The absolute values of β are relatively small ($\leq$10 μm^{-1}), as generally observed for molecules with a center of chirality as a sole stereogenic unit.[3]

The *p*-substitution in the phenyl ring seems to have only a minor effect on the twisting power: β values of compounds **2**−**5** and **6**−**9**, in which groups with different electron donor or acceptor characteristics are present, exhibit very similar values. In the only case investigated, the electronic feature of the substituent present in the benzyl ring (see **10**) is not relevant. These results seem to indicate that in the present system the short-range interactions, and not polarity/electrostatic properties, are the most important molecular characteristics in controlling the chiral induction. This is in keeping with the observation that electrostatic interactions have been proven to give minor contributions to the orientational order (and also to β), also in other compounds such as biphenyl derivatives with substituents with a strong electron-donating or -withdrawing characteristic.[14]

The most important feature emerging from the analysis of Table 1 concerns the relationship between the molecular and the phase chirality. All the investigated acyclic dopants **1**−**17** possessing (*S*)-absolute configuration transform the nematic solvents E7, Phase 1083, and ZLI 2359 into left-handed (*M*) chiral nematics. Therefore, the relation (*S*)-configuration → (*M*)-handedness is consistently observed. The behavior in the nematic solvents MBBA and Phase 1052 is, instead, more complex. While a few compounds (**1**, **11**, **14**, and **15**) exhibit the same relation observed in E7, the remaining dopants show the opposite relation: (*S*)-configuration → (*P*)-handedness. It should be noticed that in compounds **1**, **11**, **14**, and **15**, the rotation around the C_{Ar}–S is likely to be more hindered than for the other derivatives, due to the presence of ring substituents and to the size of the alkyl group bound to the sulfur. It is well-known that the handedness of the induced chiral nematic can depend on the nature of the solvent, and in some cases, opposite handedness has been found in different solvents. In particular, it has already been reported that sulfoxides may induce cholesterics of opposite handedness in MBBA and Phase IV.[25]

To have a theoretical picture of the relationship expected between the configuration of the dopant and the handedness of the induced chiral nematic, we have carried out calculations of the helical twisting power of some selected sulfoxides based on the surface chirality model.

Computations of the chirality parameter *Q* have been performed for selected geometries of a few compounds, namely for derivatives **1**, **2**, and **11**, as examples of phenyl alkyl sulfoxides, and for the naphthyl alkyl sufoxides **12**, **15**, and **16**. The stable conformations, as obtained by geometry optimization with the semiempirical PM3[26] method, are shown in Figure 1. For **1** and **11**, the presence of bulky substituents gives rise to a constrained geometry, forcing the S−O bond to be almost coplanar with the phenyl moiety. The conformations afforded by the calculation for **2**, **12**, **15**, and **16** correspond to those

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CHART 2

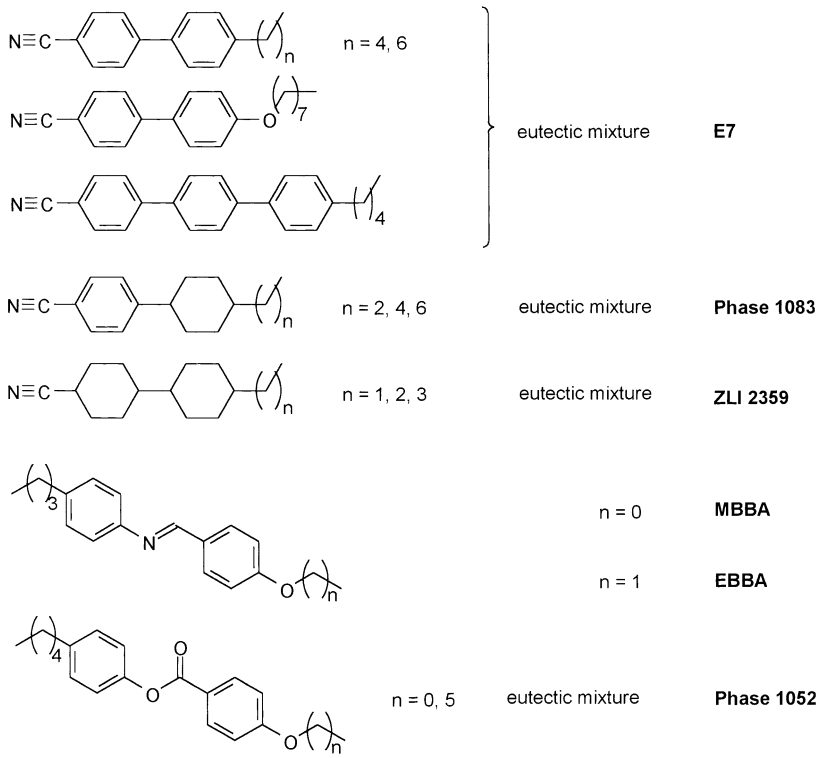

TABLE 1. *β* Values for (*S*)-Sulfoxides 1−19

		β (μm^{-1})				
compd	abs config	E7	1083	2359	MBBA	1052
1	S	−7.7	−10.6	−10.4	−8.9	−7.6
2	S	−3.2	−3.1	−2.7	+0.6	+1.1
3	S	−2.9	−3.6	−2.7	∼0	+1.0
4	S	−4.4	−5.7	−4.4	+1.1	+0.9
5	S	−3.6	−4.0	−4.0	+4.8	+1.0
6	S	−1.6			+1.9	
7	S	−3.6			+1.6	
8	S	<0			nm[a]	
9	S	−1.8			+4.3	
10	S	−1.1			+3.2	
11	S	−4.6	−2.9	−5.4	∼0	−0.4
12	S	−3.4	−2.4	−2.3	+4.1	+1.1
13	S	−3.7	−3.8	−5.9	+7.7	+5.3
14	S	−7.1			nm	−1.6
15	S	−10.4		−6.6	∼0	−2.1
16	S	−5.7	−6.2	−6.5	+1.1	∼0
17	S	−4.2	≪0	−3.5	+1.7	∼0
18	S	+1.8	+1.4	+2.0	+2.0	+1.1
19	S	+3.2			+2.9	

[a] Not measurable.

reported in ref 18. For **2**, the conformation with an efficient overlap between the $3sp^3$ orbital of the sulfur and the 2p orbital on the carbon has been considered. This conformation with the S−O bond almost eclipsed with the phenyl ring is in agreement with the spectroscopic consideration discussed in ref 18 and similar to that proposed by Benassi et al. from NMR studies.[27] Analogous conjugated conformations have been considered for the *β*-naphthyl compound **16** (Figure 1). On the other hand, owing to the steric hindrance exerted by the peri hydrogen and by the methyl group possibly present in C(2), the α-naphthyl compounds **12** and **15** are forced to adopt conformations in which the smallest group on the sulfur (the lone pair) is in the aromatic plane pointing toward the peri hydrogen or the methyl in C(2),[18] such as that reported in Figure 1.

The predicted *Q* values are summarized in Table 2. All *Q* values obtained for the acyclic sulfoxides under examination are rather low, significantly lower than those predicted for other chiral compounds previously investigated.[13−15] This is in agreement with the weak twisting powers reported in Table 1 (for a discussion between the quantitative relation between computed *Q*s and experimental *β* values, see ref 14). It is worth mentioning that, given the intrinsic approximations of the theoretical approach, such small *Q* values should be contemplated with some care, considering the general trends more than the single values, which might be affected by a significant uncertainty. We see from Table 2 that the acyclic sulfoxides with (*S*)-absolute configuration always exhibit negative *Q* values (negative *β* values) and therefore (*M*)-chiral nematics are expected. This theoretical prediction matches the behavior of the dopants observed in E7, Phase 1083, and ZLI 2359.

The knowledge of the preferred conformation is a critical point of the theoretical treatment. To get insight into the effect of the conformational changes on the sign and value of *Q* (and hence *β*), the torsional potential for the rotation about the angle $\theta_{(O-S-C-C)}$ has been calculated for derivatives **2**, **12**, and **16**. Calculations have been performed at the HF/6-31G* level; for the former compound, also DFT at the B3PW91/6-31G* level has been employed and only minor effects on the torsional profile have been observed. The profiles obtained for **2** and **16** are reported in parts A and B of Figure 2, respectively,

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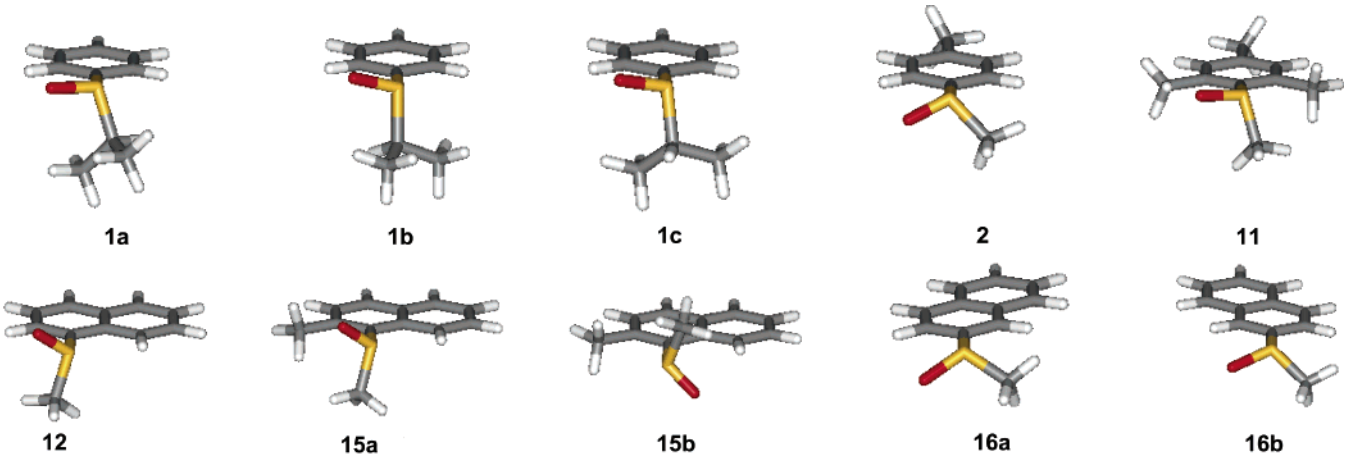

FIGURE 1. The conformations of compounds **1** (**1a**−**c**), **2**, **11**, **12**, **15** (**15a,b**), and **16** (**16a,b**) used for the calculation of *Q*.

TABLE 2. *Q* Values for Selected Geometries of a Few (*S*)-Sulfoxides

compd	abs config	conform.	Q/Å^3	compd	abs config	conform.	Q/Å^3
1a	S	Figure 1	−1.7	**16a**	S	Figure 1	−0.9
1b	S	Figure 1	−0.6	**16b**	S	Figure 1	−1.1
1c	S	Figure 1	−0.7	**18a**	S	Figure 3	+0.7
2	S	Figure 1	−0.1	**18b**	S	Figure 3	+0.4
11	S	Figure 1	−1.0	**19a**	S	Figure 3	+0.2
12	S	Figure 1	−1.8	**19b**	S	Figure 3	+0.3
15a	S	Figure 1	−2.4	**19c**	S	Figure 3	+0.4
15b	S	Figure 1	−1.1				

together with the *Q* values. In both cases, pronounced minima in correspondence to conformations with the S−O bonds almost coplanar with the aromatic plane are predicted. Also the chirality parameter *Q* shows a strong dependence on the torsional angle, changing in both compounds from negative to positive values when the S−O bond moves from the aromatic plane to the perpendicular arrangement. This means that the handedness of the induced chiral nematic is predicted to depend on the torsional angle. Analogous results, both for the torsional potential and the *Q* profile have been obtained for **12**, even though for this compound the maxima of the potential for orientations of the S−O bond pointing toward the opposite sides of the aromatic plane are significantly different.

Summarizing, we have seen that in all three cases, the dependence of the shape chirality strictly matches the energy dependence: the stable conformers exhibit the same negative shape chirality and therefore they are expected to contribute in the same way to the sign of β. This expectation is not trivial. In fact, in the framework of the exciton coupling, the two more stable conformations of **16** (see Figure 1) exhibit opposite chromophoric chirality,[18] because the transition dipole moments responsible for the optical activity in the UV region define opposite helicities. Therefore, the two conformers contribute in an opposite way to the sign of the CD spectrum and detailed knowledge of the actual conformation is necessary in order to use CD spectroscopy in the configuration assignment.

In the approximation adopted in the surface chirality method, the role of the solvent is simply to act as an orienting matrix and amplifier of the molecular chirality;

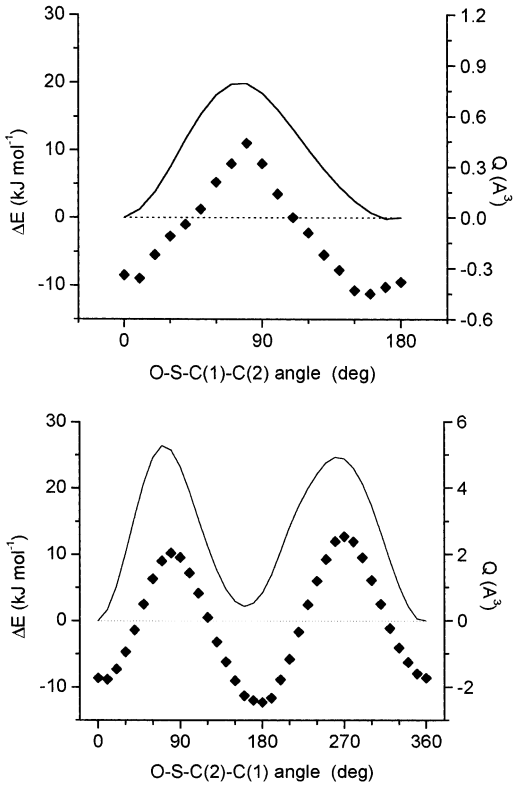

FIGURE 2. The torsional potential (solid) and the chirality parameter *Q* (dotted) for (*S*)-**2** (top) and for (*S*)-**16** (bottom) as a function of the dihedral angle O−S−C−C.

thus, perturbation of the conformational equilibrium or specific solute−solvent interactions cannot be predicted by the model. Therefore, the agreement with experimental data obtained in the case of solvents E7, Phase 1083, and ZLI 2359 seems to indicate that such solvents do not present specific interactions with the dopants and that the conformations considered in the calculations are reasonable.

A possible origin of the more complex behavior observed in MBBA and Phase 1052 can be the perturbation of the conformational equilibrium induced by these solvents. A change of the torsional potential, with a destabilization of the geometries having the S−O bond

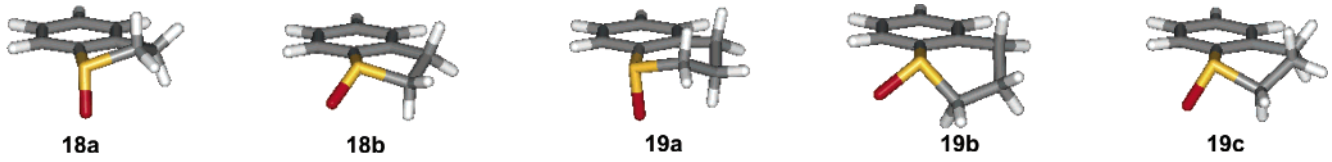

FIGURE 3. The conformations for compounds **18** (**18a,b**) and **19** (**19a**−**c**) used for the calculation of *Q*.

quasi-coplanar with the aromatic plane in favor of arrangements characterized by a perpendicular S−O bond, might be associated with a change of handedness of the induced cholesteric phase. To test this hypothesis, we measured the twisting powers of the two cyclic sulfoxides **18**−**19**. Bridging the alkyl group to the aryl group of an alkyl aryl sulfoxide leads to a less flexible structure whose conformation equilibria are easily predictable. The results are reported in Table 1. A remarkable feature is that in all solvents these (*S*)-configurated dopants induce chiral nematics of the same *right*-handedness. Values of the chirality parameter *Q* have been calculated for the most populated conformations, determined with the semiempirical PM3 method,[26] and are shown in Figure 3. The theoretical predictions, reported in Table 2, support the experimental values.

It should be noticed that the handedness induced by heterocyclic compounds **18** and **19** is opposite with respect to that induced by open-chain derivatives **1**−**17**.[28] This fact is not unexpected: the most representative conformations for the two groups of sulfoxides are quite different, the latter presenting the S−O bond not far from coplanarity with the aryl ring (see Figure 1)[20] and the former showing a more pronounced dihedral angle (see Figure 3).[21]

Going back to the open-chain derivatives, the only compounds where chiral nematics of the same handedness are induced in all solvents are **1**, **11**, **14**, and **15**. These sulfoxides share a common feature: the presence of substituents in the aromatic ring (ortho with respect to the sulfinyl group) or of bulky alkyl groups that possibly reduce the molecular flexibility. A further confirmation of the role of the conformational equilibria in determining the different solvent behavior of **1**, **11**, **14**, **15**, **18**, and **19** with respect all other dopants can be obtained by observing the temperature dependence of the pitch for some selected compounds. We measured the variation of the pitch with temperature for **2**, as representative of the more flexible molecules, and of **18**, as representative of the less flexible ones, in E7 and in the mixture MBBA/EBBA 1:1.[29] The results are reported in Figure 4.

The temperature dependence of the pitch of a chiral nematic, $p(T)$, is an important property on which several applications are based (e.g., thermography).[30] In most pure cholesteric materials (i.e., chiral nematics formed

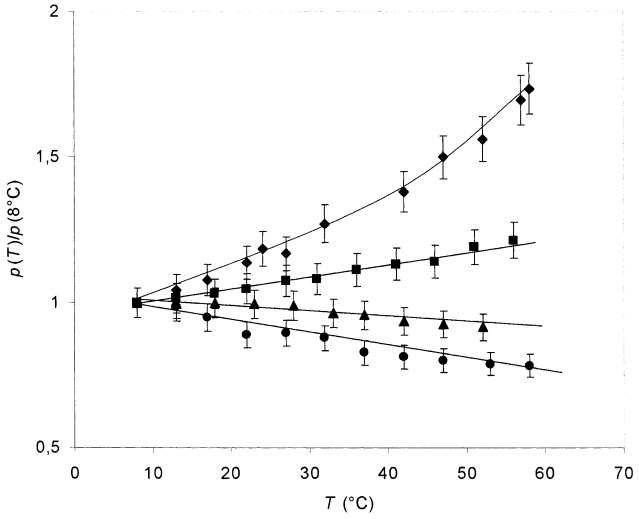

FIGURE 4. Normalized pitches ($p_T/p_{8°C}$) as a function of temperature: Diamond, **2** in MBBA/EBBA 1:1; square, **2** in E7; triangle, **18** in MBBA/EBBA 1:1; circle, **18** in E7.

by chiral nonracemic compounds), the pitch is a decreasing function of the temperature. However, in chirally doped nematics, both an increase and a decrease of the pitch with temperature and even helix inversions have been observed, depending on the nature of the dopant.[31−33] A comprehensive theory of the temperature dependence is yet to be developed,[34] and several factors may be responsible for the temperature dependence of the twist; among these, variations of the order (as expressed by the ordering tensor **S**), of the elastic response of the solvent to the twist (K_{22}), and of conformation seem to be relevant.[7,33,35]

In the case where the dopant is highly anisometric, the local order is not affected very much by the presence of the dopant and a simplified description of the $p(T)$ dependence of a doped nematic has been proposed:[33] the reduction of the nematic K_{22} with temperature[36,37] favors the helical twisting and a decrease of p is observed.

Positive dp/dT has been attributed to low-anisometric dopants strongly disturbing the local ordering in the mesophase (by increasing temperature, this effect over-

(28) It is interesting to note that open-chain alkyl aryl sulfoxides and their cyclic counterparts, having the same absolute configuration, show electronic CD spectra that are almost in a mirror image relationship. See: Devlin, F. J.; Stephens, P. J.; Scafato, P.; Superchi, S.; Rosini, C. *Chirality* **2002**, *14*, 400.

(29) This mixture has been used instead of pure MBBA in order to extend the temperature range of existence of the nematic phase (T_i = 59 °C). The β values measured at room temperature in MBBA and in MBBA/EBBA 1:1 are, within the experimental error, the same.

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whelms the concomitant effect due to the K_{22} reduction[33]) and to modifications of the conformational equilibria occurring during the *T*-scanning. Significant change in the pitch during heating have been explained in terms of changes of molecular conformation for binaphthyl derivatives by Deussen et al.[35] and with a statistical model based on the Boltzmann distribution between two states (conformations) for flexible molecules by Chilaya et al.[32]

A negative d*p*/d*T* has in fact been observed for **18** in E7 and in MBBA/EBBA. A more negative value of d*p*/d*T* in E7 in comparison with that in MBBA/EBBA (having a weaker K_{22} vs *T* dependence[36,37]) is in agreement with a $p(T)$ dependence mainly controlled by the temperature dependence of K_{22}.

The temperature dependence observed for **2** in both solvents is of the opposite type (pitch increases with temperature) and is extremely pronounced in the case of the mixture MBBA/EBBA. Such results support our hypothesis of the importance of the torsional freedom for the more flexible derivatives. The results obtained in E7 can be easily explained by considering that the increase of temperature is accompanied by an increase in the dynamic conformational disorder or, in other words, by a broadening of the Boltzmann distribution around the minima of the torsional potential. Since, as appears from Figure 2, moving away from the minima, lower *Q* values are predicted, the increase of temperature is expected to produce an increase of the helical pitch. The change of handedness and the high slope of the curve *p* vs *T* in MBBA/EBBA could be consistent with the occurrence of a second and lower minimum in the torsional potential, in correspondence to a conformer with the S−O bond far from the aromatic plane, and thus with a positive twisting power. The relative weight of the other conformer, with negative β value, would increase with temperature, thus leading to an overall weakening of the twisting ability, i.e., an increase of the helical pitch. However, calculations in a vacuum give no evidence of a second minimum in the torsional potential, and presently we can only speculate its appearance as an effect of interactions with the solvent.

Conclusions

The coupling of the experimental determination of the helical twisting powers of chiral dopants with a theoretical analysis of their molecular properties (anisometry and chirality of the molecular surface) is a powerful method for assigning absolute configuration. In this paper, we have reported this approach to assess, for the first time, the configuration of alkyl aryl sulfoxides, molecules whose chirality originates in a single center of chirality.

In the nematic solvents E7, Phase 1083, and ZLI 2359, all (*S*)-open chain alkyl aryl sulfoxides induce (*M*)-chiral nematics, whereas the chemically related (*S*)-cyclic sulfoxides induce, in the same solvents, (*P*)-chiral nematics. This different behavior is mainly connected to the different conformations present in the two class of dopants: in the open-chain compounds, the S−O bond is close to coplanarity with the aryl group, while in the cyclic sulfoxides, the S−O bond is almost perpendicular to the aryl moiety.

The most important result of this paper is that even in the case of small β values, a reliable assignment of absolute configuration can be established by comparison of the theoretical and experimental helical twisting power. However, it must be kept in mind that the predictions of the present theoretical model are reliable only in the case of shape-dependent interactions between the solute and the solvent and when no (even weak) specific interactions are present between them. Therefore, in the case of small β values, it is necessary to use nematic solvents (e.g. the biphenyl ones) that minimize specific interactions with the solute and do not modify its conformational equilibrium with respect to that calculated in a vacuum.

Experimental Section

General Procedures. Cholesteric pitches and handednesses have been obtained using the lens version of the Grandjean−Cano method.[38] The helical twisting powers of the (*S*)-enantiomers have been calculated through eq 1: the measurements were carried out on the enantioenriched compounds and corrected to 100% ee. The technique is described in detail in ref 39. Nematic solvents used are commercial products (see Chart 2 for the chemical structures): MBBA, T_i = 47 °C; EBBA, T_i = 68 °C; E7, T_i = 60 °C; ZLI 2359, T_i = 68°C; Phase 1052, T_i = 48 °C; Phase 1083, T_i = 52 °C.

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ using TMS as internal standard. Optical rotations were measured with a digital polarimeter. Enantiomeric excesses of the sulfoxides were determined by HPLC on Daicel Chiralcel OD, OB, and OJ columns.[23] CCl_4 was distilled from CaH_2 and stored over activated 4 Å molecular sieves. Ti(*i*-PrO)$_4$ was distilled prior to use under N_2 atmosphere. Commercially available *tert*-butyl hydroperoxide (TBHP) (70% in water) was used as purchased. The preparation of sulfoxides **1**−**8**, **12**, **13, 15**−**17**, and **19** has been described elsewhere.[20−23] Compounds **9**−**11**, **14**, and **18** have been prepared by enantioselective oxidation[22] of the corresponding sulfides and showed analytical and spectroscopic data in full agreement with the reported structure.

Calculations. Optimized geometries and potential energy profiles are obtained by ab initio and semiempirical methods, as implemented in the Gaussian 98 package.[26] The chirality parameter *Q* is calculated with a homemade code, based on the following procedure.[8,9] (1) Given the nuclear positions, the molecular surface is generated. This is defined as the surface drawn by the center of a bead rolling on the assembly of van der Waals spheres centered on the nuclei[40] and is approximated by a set of triangles, obtained with the algorithm developed by Sanner et al.[41] (2) The **T** and **Q** tensors, related respectively to the anisometry and the chirality of the molecular surface, are calculated by summing the contributions from all the triangles. (3) The elements of the Saupe ordering matrix **S** are calculated as averages over all molecular orientations:

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

where φ denotes the angles between the molecular axes (*i*,*j*) and the local director, and $U(\varphi)$ is the orienting potential

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experienced by the molecule in the nematic phase

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

Finally the chirality parameter Q is obtained according to eq 3.

Representative Procedure for Oxidation of Sulfides.[22] (*S*)-(−)-1-Naphthylisopropyl Sulfoxide (14). To a suspension of (*R*,*R*)-1,2-diphenylethane-1,2-diol (21.4 mg, 0.1 mmol) in CCl_4 (3 mL) were added dropwise in sequence Ti(*i*-PrO)$_4$ (15.0 μL, 0.05 mmol) and H_2O (18.0 μL, 1.0 mmol). To the resulting homogeneous solution, 1-naphthylisopropyl sulfide (202 mg, 1.0 mmol) was added and stirring continued for 15 min at room temperature. The solution was then cooled at 0 °C and TBHP (70% in water, 274 μL, 2.0 mmol) added. The mixture was left stirring at 0 °C for 2 h and then diluted with CH_2Cl_2 and dried over Na_2SO_4. After filtration and evaporation of solvent, the residue was purified by column chromatography (silica gel; EtOAc), isolating pure (−)-**14** (104 mg, 48%) as a clear liquid: ee = 22%; $[\alpha]_D = -89.5$ (c = 1.33, acetone); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.16 (d, J = 6.7 Hz, 3H), 1.24 (d, J = 6.7 Hz, 3H), 2.93 (m, 1H), 7.4−7.6 (m, 4H), 7.67 (d, J = 6.6 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 8.52 (d, J = 8.3 Hz, 1H).

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