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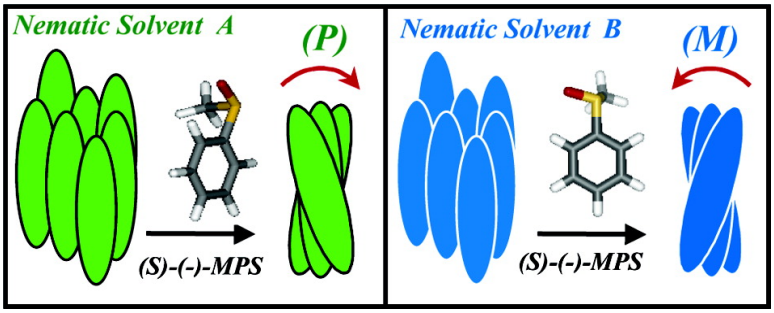
J. Am. Chem. Soc., **2005**, 127 (33), 11736-11744• DOI: 10.1021/ja051589a • Publication Date (Web): 29 July 2005



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Solute−Solvent Interactions and Chiral Induction in Liquid Crystals

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Abstract: The induction of a cholesteric phase by doping an achiral nematic liquid crystal with an enantiopure solute is a phenomenon that, as in all general supramolecular phenomena of chiral amplification, depends in a subtle way on intermolecular interactions. The micrometric helical deformation of the phase director in the cholesteric phase is generated by the interplay of anisotropy and chirality of probe−medium interactions. In the case of a flexible chiral dopant, the solvent can influence the twisting power in two ways, difficult to disentangle: it is responsible for the solute orientational order, an essential ingredient for the emergence of phase chirality; but also it can affect the dopant conformational distribution and then the chirality of the structures present in the solution. In this work we have investigated methyl phenyl sulfoxide, a flexible, chiral molecule that, when dissolved in different nematics, can produce cholesteric phases of opposite handedness. This peculiar, intriguing sensitivity to the environment makes MPS a suitable probe for a thorough investigation of the effects of solute−solvent interactions on chiral induction in liquid crystals. NMR experiments in various nematic solvents have been performed in addition to twisting power measurements. From the analysis of partially averaged $^{1}H-^{1}H$ and $^{13}C-^{1}H$ dipolar couplings, the effects of solvent on solute conformation and orientational order are disentangled, and this information is combined with the modeling of the chirality of intermolecular interactions, within a molecular field theory. The integration of different techniques allows an unprecedented insight into the role of solvent in mediating the chirality transfer from molecule to phase.

1. Introduction

Chiral nonracemic dopants, when dissolved in nematic solvents, have the ability of inducing a helical deformation of the mesophase director on the length scale of micrometers.[1] The resulting chiral nematic (cholesteric) phase is characterized by the magnitude and sign of the helical pitch p. For dilute solutions the wavenumber $q = 2\pi/p$ is a linear function of the solute molar fraction x and the enantiomeric excess r:

$$q = 2\pi/p = 2\pi\beta\, rx \qquad (1)$$

The proportionality factor β is called the helical twisting power (HTP) and is a specific function of the solute−solvent pair. It is taken as positive or negative, according to the handedness (right or left, respectively) of the cholesteric helix.[2] The study of induced cholesteric phases has led to relevant information about the stereochemistry of dopants, the main goal being the understanding of the relation between the cholesteric handedness and a stereochemical descriptor of the molecular chirality.[3] In a macroscopic picture, cholesteric induction can be explained in terms of the competition between the chiral strength, which favors a twist deformation of the mesophase director, and the elastic restoring torque, which opposes the deformation.[4] The latter contribution is amenable to measurement and can be considered a property of the liquid crystal solvent at the given temperature, at least for dilute solutions. On the contrary, the chiral strength depends on the solute−solvent pair, and a molecular statistical analysis allows its interpretation in terms

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(2) (a) Solladié, G.; Zimmermann, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 348. (b) Baessler, H.; Labes, M. M. *J. Chem. Phys.* **1970**, *52*, 631. (c) Spada, G. P.; Proni, G. *Enantiomer* **1998**, *3*, 301.
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10.1021/ja051589a CCC: $30.25

of chirality and anisotropy of solute−solvent interactions.[5,6] In this sense HTP can be viewed as a sensitive probe of intermolecular forces, reflecting features, like their anisotropy, which are not accessible by experiments in isotropic liquids, where anisotropies are completely washed out. Unfortunately the experimental observable conveys only average information on the interplay between chirality and anisotropy of the interactions experienced by a given solute. Therefore the understanding of the molecular mechanism requires a theoretical analysis, with a detailed modeling of solute and solvent, as needed when dealing with chiral properties. Actually, it has been seen that in most cases the twisting ability scales with solvent in a similar way for different chiral dopants. This has suggested that the specific features of solvent should play a minor role in the phenomenon of chiral induction in liquid crystals. Namely, a simple interpretation of the experimental behavior can be gained in terms of a phenomenological model, wherein chirality and anisotropy of interactions are parametrized in terms of those of the molecular surface of the dopant, while solvent only enters through its macroscopic properties, i.e., orienting strength and twist elastic constant.[5]

Recently, a strong solvent dependence of the helical twisting power, comprising changes in handedness, has been observed for a set of flexible alkyl aryl sulfoxides.[7] It was seen that in cyanobiphenyl, cyanophenylcyclohexyl, and cyanobicyclohexyl solvents these dopants induce chiral nematic phases of handedness opposite to that observed in phenylbenzoate and benzylideneaniline solvents. This fact clearly reflects changes in solute−solvent interactions. A reason for the high solvent sensitivity of the HTP of alkyl aryl sulfoxides probably resides in their structure, characterized by the simultaneous presence of an aromatic ring and a nonnegligible electric dipole along the SO bond, which can rotate with respect to each other. In the case of rigid alkyl aryl sulfoxides a different behavior was observed, with homochiral cholesteric phases induced by a given enantiomer: this suggested that changes of cholesteric handedness with solvent might originate from variations in the torsional potential about the OS−CC bond.

In this paper we report on a more systematic investigation, which has been carried out with the purpose of getting a deeper insight into the role of solvent in chiral induction. We have focused on methyl phenyl sulfoxide (MPS): this compound, which was not considered in the past studies,[7] is the simplest member of the series of flexible alkyl aryl sulfoxides. The HTP of the *S* enantiomer has been measured in various liquid crystal solvents, chosen for their different structure and dielectric properties. In addition, an extensive liquid crystal NMR (LXNMR) analysis has been performed on MPS with ^{13}C-labeled methyl group, a strategic position for conformational investigations; henceforth we will refer to this molecule as MPS-13C. NMR in partially ordered phases is a powerful tool for the conformational analysis of solutes: the spectra of $^1/_2$ spin nuclei (typically, ^{1}H and ^{13}C) are strongly affected by dipolar (or direct) couplings D_{ij}, representing a rich source of structural, conformational, and orientational information since they are directly related to the magnitude and orientation of internuclear vectors connecting the interacting nuclei (see Appendix, section A2, in the Supporting Information). For this reason reduced dipolar couplings are also used for the structure determination of proteins.[8] In the case of small molecules as MPS, if a sufficient number of magnetically active nuclei is available, both the torsional potential and the order parameter (or Saupe) matrix **S** can be obtained as a function of the torsional angle by fitting the experimental data.[9] This detailed knowledge allows us to disentangle the effect of solvent on torsional potential and orientational order. The information derived from NMR has been used within a molecular theory connecting HTP with the orientational order and chirality of MPS; the latter is calculated as a function of the torsional angle according to the surface chirality method.[5]

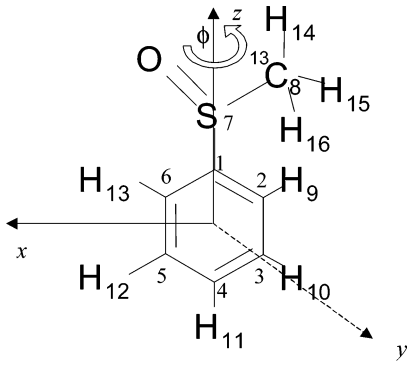

Figure 1. The molecule of ^{13}C-labeled methyl phenyl sulfoxide (MPS) with the reference system (x,y,z) and the torsional angle ϕ with its positive sense of rotation. The value $\phi = 0$ is assumed for the S−O bond in the plane of the aromatic ring.

The body of the paper has been organized in order to favor the illustration of results, avoiding detailed descriptions of important, but perhaps boring, technical aspects; these have been moved to a long Appendix available in the Supporting Information, where interested readers will find all details (for the sake of brevity, henceforth the frequent calls to the Appendix will be shortened in this way: App. − s. A*n* − in the SI; where App. is for Appendix, s. A*n* indicates the *n*-th section of Appendix, and SI is, of course, for Supporting Information).

2. Results and Discussion

2.1. NMR Experiments and Analysis. NMR experiments (see Experimental Section) have been carried out at room temperature on the racemic mixture of MPS-13C (Figure 1) dissolved in the achiral nematic solvents ZLI-1132, EBBA, and CCN55 (Chart 1). These nematics, beside being well-known and widely used as solvents for NMR studies,[9] are also representative of the classes of liquid crystals used for HTP measurements (see section 2.2). The results obtained for the racemic compound can be extended to the enantiopure dopant in the induced cholesteric phase. In fact, the NMR spectra in the achiral nematic phases, as well as all nonchiral properties, are identical for the two enantiomers; furthermore, the cholesteric pitch has a length of the order of micrometers, and the cholesteric phase induced by a given enantiomer is locally very similar to the nematic phase formed by the racemic mixture.

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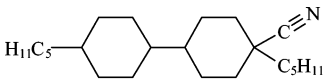
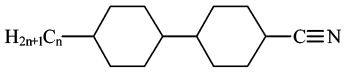
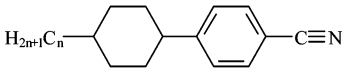
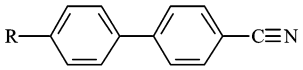
(9) Celebre, G.; Longeri, M. In *NMR of Ordered Liquids*; Burnell, E. E., de Lange, C. A., Eds.; Kluwer: Dordrecht, 2003.

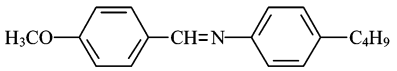
Chart 1

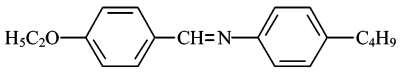
CCN55 

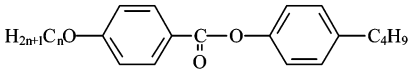
ZLI-2359  n = 2, 3, 4

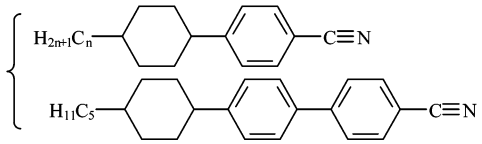
ZLI-1083  n = 3, 5, 7

E7  R = C_5H_{11}, C_7H_{15}, OC_8H_{17}, *p*-$C_5H_{11}Ph$

MBBA 

EBBA 

ZLI-1052  n = 1, 6

ZLI-1132  n = 3, 5, 7

Experimental and calculated spectra of MPS-13C are shown in Figure 2. Their analysis was carried out in stages, with an iterative procedure (see App. − s. A1 − in the SI): the chemical shifts obtained in this way and the partially averaged D_{H-H}, D_{C-H} dipolar couplings are reported in Table 1. The D_{ij}'s in CCN55 are all positive, and most of them are smaller in magnitude than those observed in the other solvents: this is due to the fact that the director aligns perpendicular to the magnetic field in CCN55 and parallel to it in the other solvents (the diamagnetic anisotropy $\Delta\chi$ is negative for CCN55, while it is positive for EBBA and ZLI-1132).[10]

The measured D_{ij} dipolar couplings are averages over all possible molecular conformations, defined by the torsional angle ϕ, and all orientations of the molecule relative to the external applied magnetic field B_0. They can be expressed in the following form:[9]

$$D_{ij} \equiv \tilde{D}_{ijZZ} = \left[\frac{1}{2}(3\cos^2\alpha - 1)\right] \cdot \left[\frac{2}{3}\sum_{\varsigma}\int S_{\varsigma\varsigma}(\phi)\, D_{ij,\varsigma\varsigma}(\phi)\, p(\phi)\, d\phi\right] \quad (2)$$

where α is the angle between B_0, defining the Z direction in the laboratory frame, and **n**, the director of the mesophase. The function $p(\phi)$ is the torsional angle probability distribution, and $S_{\zeta\zeta}(\phi)$'s are the principal elements of the Saupe matrix **S** describing the alignment of MPS to the nematic director.[4]

The element $S_{\zeta\zeta}(\phi)$ is a function of the solute conformation, since in general both the degree of alignment and the alignment axes vary when conformation is changed. The $D_{ij,\varsigma\varsigma}(\phi)$'s represent the corresponding Cartesian components of the dipolar coupling tensor between the *i* and *j* nuclei. This tensor depends on the molecular conformation if the two nuclei are located in different moieties of the solute, i.e., one in the methyl and the other in the aromatic group. Elements of the dipolar coupling tensors are calculated on the basis of the molecular geometry (see App. − s. A3 − in the SI), whereas elements of Saupe matrices, $S_{\zeta\zeta}(\phi)$, and torsional angle distributions in the nematic phases, $p(\phi)$, are derived from a fit of the partially averaged dipolar couplings by assuming a model for their dependence upon the ϕ angle. The methodology, based on the application of the so-called additive potential (AP) model, has been presented elsewhere,[9] and it is summarized in App. − s. A2 − in the SI. In short, within this approach the torsional potential is expressed as a superposition of an isotropic part, which would be present in a virtual isotropic phase of the nematic solvent at the experiment temperature and a term accounting for how well a given conformation can be accommodated in the nematic environment. The latter is approximated as the sum of independent contributions from each "rigid" moiety in the molecule.

The AP method has been criticized[11,12] because it suffers, in principle, from a drawback (see App. − s. A2 − in the SI, for a detailed discussion). Anyway, this drawback could become really serious in particular when very flexible solutes (with many torsional degrees of freedom, as, for example, long alkyl chains) are treated: for such systems other models (as, e.g., the Chord Model[12]) can be used. On the other hand, as well testified by a wide range of literature in the field, the AP model has been

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(12) Samulski, E. T. In *NMR of Ordered Liquids*; Burnell, E. E., de Lange, C. A., Eds.; Kluwer: Dordrecht, 2003.

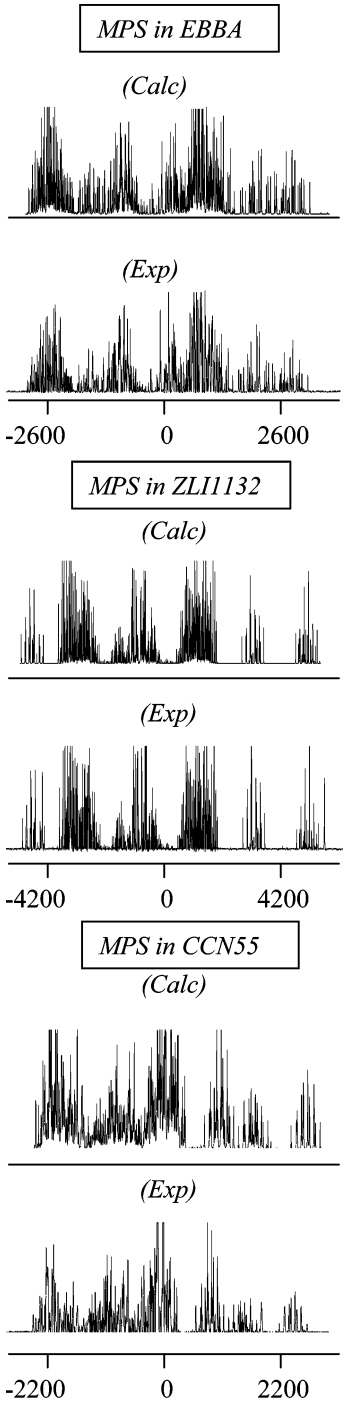

Figure 2. Experimental and calculated ^{1}H-LXNMR spectra of MPS-13C in the nematic solvents EBBA, ZLI-1132, and CCN55.

largely used in the past, and it proved its effectiveness and reliability (also compared with results from other techniques) especially when small flexible molecules were studied (see, e.g., ref 9 and reference therein, where, inter alia, the cases of anisole and ethylbenzene are illustrated). Since, in the present work, we deal with MPS, a very small flexible molecule with, in practice, just one torsional degree of freedom, AP can represent an effective method to treat the case.

The orientational and conformational analysis has been carried out as described in App. − s. A4 − in the SI. It is worth emphasizing that, from the use of the AP model in analyzing NMR dipolar couplings, also the probability distribution in a

Table 1. Chemical Shifts and Dipolar Couplings of MPS-13C in ZLI-1132, EBBA, and CCN55

$\{D_{ij}\}/\{\text{Hz}\}$	MPS-13C in ZLI1132	MPS-13C in EBBA	MPS-13C in CCN55
$D_{9,10}$	-1543.36 ± 0.06	-896.45 ± 0.14	630.57 ± 0.18
$D_{9,11}$	-231.55 ± 0.19	-115.23 ± 0.41	96.83 ± 0.61
$D_{9,12}$	-61.53 ± 0.06	0.13 ± 0.16	26.19 ± 0.24
$D_{9,13}$[a]	-24.18 ± 0.08	60.37 ± 0.16	14.91 ± 0.24
$D_{9,14}$	-77.17 ± 0.12	-99.15 ± 0.21	66.30 ± 0.25
$D_{10,11}$	-474.03 ± 0.17	6.72 ± 0.29	210.62 ± 0.67
$D_{10,12}$[a]	-24.18 ± 0.08	60.37 ± 0.16	14.91 ± 0.24
$D_{10,14}$	-95.45 ± 0.12	-61.42 ± 0.21	48.61 ± 0.26
$D_{11,14}$	-82.24 ± 0.05	-51.63 ± 0.09	40.26 ± 0.14
$D_{14,15}$	-1477.79 ± 0.03	-506.06 ± 0.06	548.02 ± 0.08
$D_{8,9}$	-42.72 ± 0.31	-31.84 ± 0.58	24.16 ± 0.69
$D_{8,10}$	-27.55 ± 0.31	-15.72 ± 0.44	14.92 ± 0.63
$D_{8,11}$	-23.86 ± 0.13	-14.83 ± 0.19	11.40 ± 0.37
$D_{8,14}$	-1146.44 ± 0.07	-378.06 ± 0.10	427.52 ± 0.17
$\{\Delta\nu_{ij}\}/\{\text{Hz}\}$	MPS-13C in ZLI1132	MPS-13C in EBBA	MPS-13C in CCN55
9,11	-77.37 ± 0.18	-71.16 ± 0.40	117.81 ± 0.44
10,11	-83.55 ± 0.19	-100.34 ± 0.29	45.98 ± 0.41
14,11	-1371.51 ± 0.05	-2190.79 ± 0.09	-1482.74 ± 0.23

[a] $D_{9,13} = D_{10,12}$ assumed.

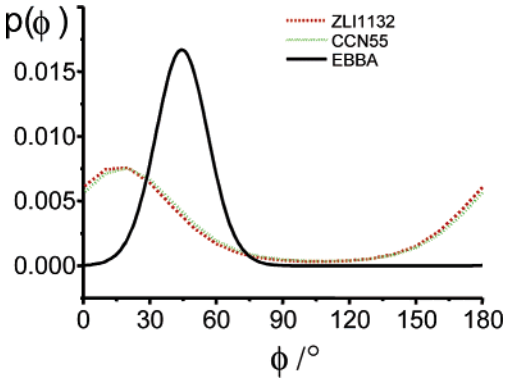

Figure 3. Probability distribution $p(\phi)$ for the OS−CC dihedral angle of MPS in the nematic phase of the solvents EBBA, ZLI-1132, and CCN55.

virtual isotropic phase of the nematic solvent at the experiment temperature, denoted as $p_{iso}(\phi)$, can be derived.[9] This corresponds to the torsional angle distribution devoid of effects of orientational order, as would be in a conventional liquid sharing the same physical properties of the nematic solvent (average dielectric permittivity, density, etc.) with the exception of the ordering power. Although $p_{iso}(\phi)$ is in principle different from $p(\phi)$ (see eq A2.12, App. − s. A2 − in the SI), for small molecules the differences have been generally found to be small[13] or negligible.[14] Also for MPS we have found $p_{iso}(\phi) \approx p(\phi)$: this indicates that orientational order has only minor effects on the conformational distribution.

The conformational distributions satisfy the relation $p^S(\phi) = p^R(-\phi)$ where the apexes denote the *S* and *R* enantiomers; their plots in the three solvents are shown in Figure 3 (there and in the following only the range 0°−180° will be shown, because of the symmetry of the torsional potential with respect to the aromatic plane).

The torsional angle distribution is found to be practically the same in both the cyano derivatives ZLI-1132 (a solvent with

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(14) Celebre, G.; De Luca, G.; Longeri, M.; Pileio, G.; Emsley, J. W. *J. Chem. Phys.* **2004**, *120*, 7075.

longitudinal dipole, $CN_{||}$) and CCN55 (a solvent with transverse dipole, $CN_{\perp}$), with maxima corresponding to conformers with the S−O bond close to the ring plane. Potential energy minima for conformations with the S−O bond approximately in the ring plane are also predicted by quantum mechanical calculations in vacuo.[7] So, the CN liquid crystals, irrespective of CN-dipole direction, do not seem to strongly perturb ϕ_{min}, the position of the minimum in the torsional potential. On the contrary, theoretical calculations[15] give an energy barrier of 34 kJ/mol, by far higher than the value obtained in our CN solvents, which is about 4 kJ/mol (Table A3, App. − s. A4 − in the SI). The torsional distribution obtained for EBBA is different from that for CN solvents, being characterized by a pronounced maximum for conformations with the aromatic ring roughly bisecting the O−S−CH_3 angle. The height of the barrier in EBBA (15 kJ/mol) is larger than that in CN solvents but still significantly lower than the value predicted in vacuo. Even considering that the fitted torsional potential is less accurate in regions corresponding to low probability conformations, the results obtained in all the investigated solvents indicate that the MPS minimum energy conformations in solution are less confined than those predicted by calculations for an isolated molecule. In ref 15 the authors themselves maintain that their theoretical energy barrier V_2 is probably overestimated with respect to experimental results in solution (ref 15 and references therein); nevertheless, the significant differences found between our values of V_2 and ϕ_{min} from different liquid crystals (Table A3, App. − s. A4 − in the SI) and theory have prompted us to a series of checks to validate the reliability of the results obtained. To do this, a large number of tests has been performed (see App. − s. A4 − in the SI, where the results of the tests are given in detail): the tests confirm the full inadequacy of theoretical values of V_2 and ϕ_{min} to fit experimental dipolar couplings and the substantial differences among the three nematic solvents.

The results obtained for MPS suggest that in this case electrostatic interactions with solvent do not strongly affect the torsional potential: ZLI-1132 and CCN55, having very different electrostatic characteristics, share indeed the same conformational distribution $p(\phi)$. About MPS in EBBA, a possible explanation for the non-negligible differences with the other solvents (mainly concerning the shape of the probability distribution function and the location of the conformational minima) lies, in our opinion, in short-range solute−solvent interactions, essentially consisting in steric repulsions, which strongly depend on the geometry of the interacting molecules.

The second piece of information derived from the LXNMR analysis concerns the orientational order of the solute in nematic solvents. The Saupe matrix **S** accounts for the degree of alignment (magnitude of the principal values) and the preferred orientations of the solute (direction of the principal axes) in the liquid crystal environment. Both depend on the solute conformation. We shall denote the principal alignment axes of a given conformer as *a*,*b*,*c*, with the labels chosen so that $S_{cc} \geq S_{aa} \geq S_{bb}$. This means that a molecule tends to orient in such a way that the director lies on the *ac* plane, with preference for alignment of the *c* axis, while the *b* axis tends to stay perpendicular to the director. The orientational behavior of a given conformer can be classified as rodlike if the largest (in magnitude) element of the Saupe matrix is positive or disklike if it is negative. For a pure rod it would simply be $S_{cc} = -2S_{aa} = -2S_{bb}$, whereas for a pure disk it would be $S_{bb} = -2S_{aa} = -2S_{cc}$. Figure 4 shows the principal elements of the Saupe matrix in the three solvents as a function of the torsional angle ϕ. Figure 5 displays the principal axes of the Saupe matrixes obtained for three selected values of the torsional angle ϕ, that is $\phi = 10°$ and $\phi = 50°$, which correspond to high probability conformations respectively in CN solvents and in EBBA, in addition to $\phi = 100°$. We can see that the degree of alignment and alignment axes are quite different in the three solvents. It appears from the plots in Figure 4 that MPS has a significantly lower degree of order in EBBA, which cannot be ascribed to a higher value of the reduced temperature $T_r = T/T_{NI}$, since the spectra were recorded at room temperature and the nematic−isotropic transition temperatures T_{NI} are quite similar (339, 342, and 345 K for CCN55, EBBA, and ZLI-1132, respectively). This implies that the T_r values are very close (in particular, T_r (CCN55) ≈ 0.88; T_r (EBBA) ≈ 0.88; T_r (ZLI1132) ≈ 0.87), and this condition justifies a direct comparison of conformational and orientational behaviors in the different solvents.

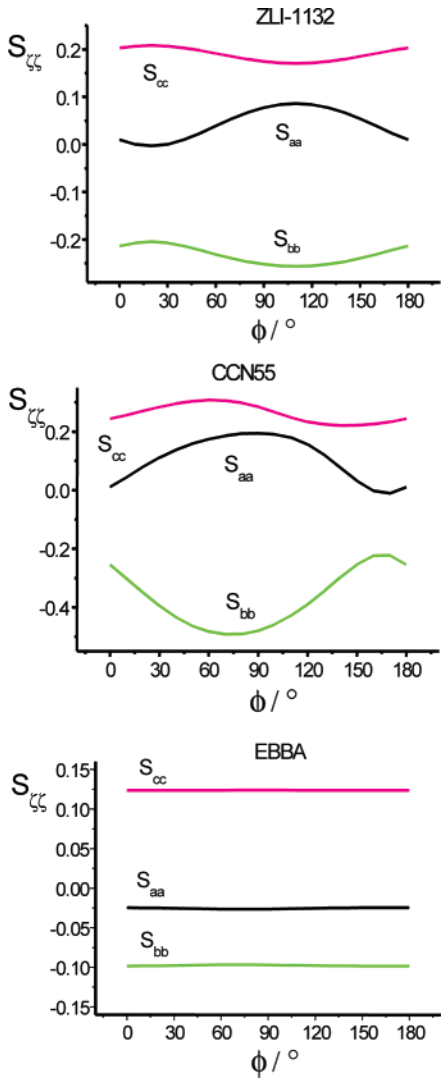

Figure 4. Principal values of the ordering matrix of MPS as a function of the torsional angle ϕ, as obtained from the NMR measurements in the solvents ZLI-1132 and CCN55 and EBBA.

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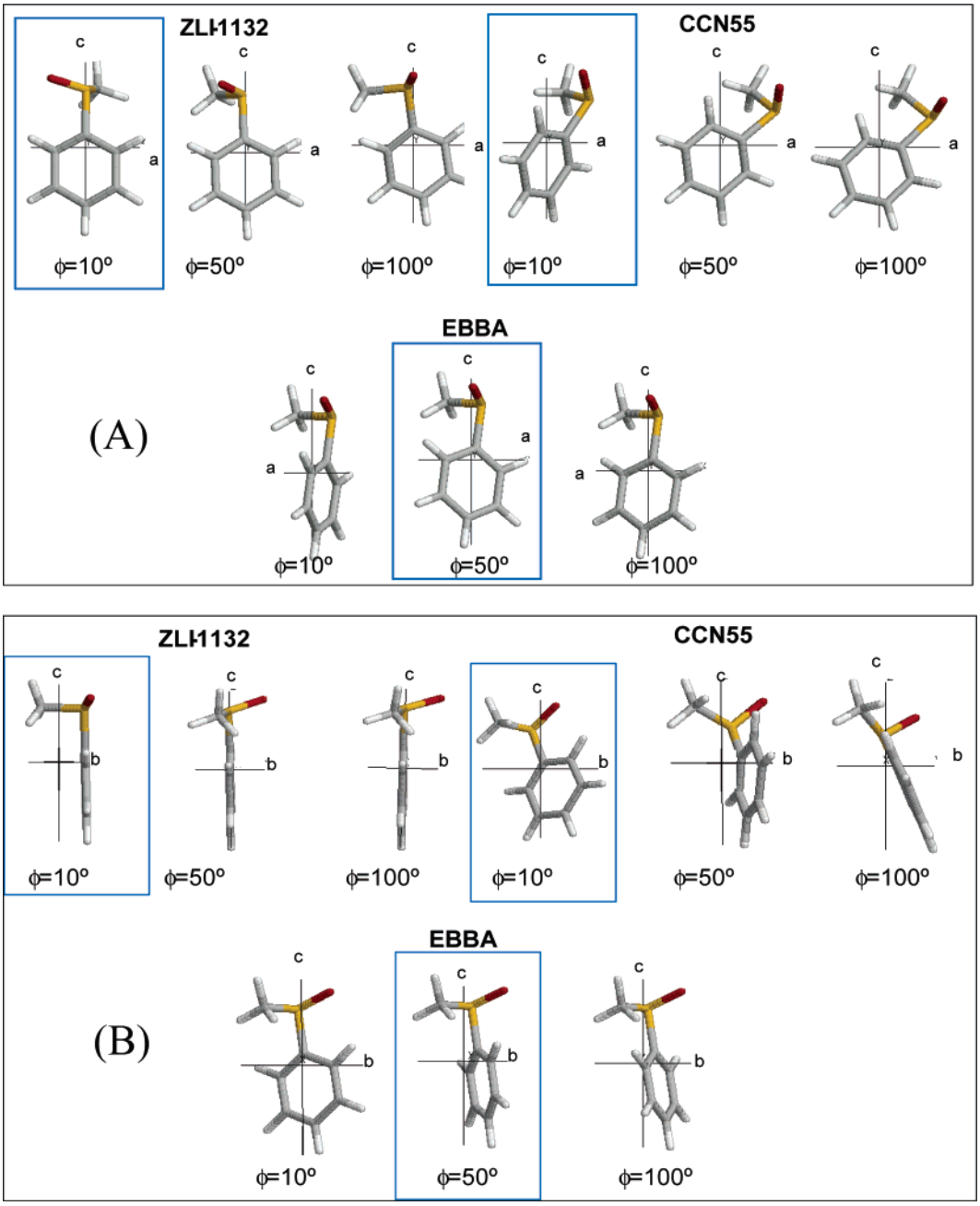

Figure 5. Principal alignment axes of MPS at selected values of the torsional angle, $\phi = 10°$, $\phi = 50°$, and $\phi = 100°$, as obtained from the NMR measurements in the nematic solvents ZLI-1132, CCN55, and EBBA. The planes *ac* (panel **A**) and *bc* (panel **B**) are shown; the *b* axis tends to lie perpendicular to the local director and along the helix axis in the chiral nematic phase. The framed structures correspond to high probability conformations in the three solvents.

The plots in Figure 4 indicate a clear rodlike behavior of the solute in EBBA; the projections in Figure 5 show that in this solvent the axis of preferential alignment to the director is not far from the Ph−S bond, irrespective of the conformation. The direction of the other principal alignment axes in the molecule changes with conformation, in such a way that the *b* axis, which has the strongest tendency to lie normal to the director, remains roughly parallel to the SO bond. On the contrary, when MPS is dissolved in the CN solvents, a basically disklike orientational behavior appears from Figure 4, along with a more pronounced dependence of alignment on the molecular conformation (rod/disk changes in solute's ordering, on passing from the solvent EBBA to the solvent ZLI-1132, were also found in the past for small rigid molecules such as 1,4-difluorobenzene and *p*-benzoquinone[16]). In ZLI-1132 a strong difference in the alignment of the three axes (large biaxiality) is observed, and Figure 5 shows a definite preference of the director to lie on the plane of the aromatic ring. An even clearer disklike behavior emerges from the plot of order parameters in CCN55, with only a small preference for alignment to the director of the *c* over the *a* axis. Moreover, Figure 5 shows that the orientation of the (*ac*) plane, which preferentially lies parallel to the nematic director, strongly depends on the molecular conformation; in contrast to the other two solvents, the orientation of the *c* axis can be far from parallel to the Ph−S bond. The difference between ZLI-1132 and CCN55 in orienting MPS probably has to be ascribed to

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Table 2. Helical Twisting Power (*S* Enantiomer) and Chirality Parameter $\bar{Q}$ (Obtained as Described in the Text), for MPS in Different Solvents

	$\beta/\mu m^{-1}$	$\bar{Q}/Å^3$
cyanophenylcyclohexyl	−2.0 (ZLI-1132) −2.3 (ZLI-1083)	<0[a] (ZLI-1132)
benzylideneaniline	+0.4 (MBBA/EBBA)	+0.7 (EBBA)
$CN_{\perp}$-cyanobicyclohexyl	+1.3 (CCN55)	+3.5 (CCN55)
$CN_{\parallel}$-cyanobicyclohexyl	−2.7 (ZLI-2395)	
$CN_{\parallel}$-cyanobiphenyl	−2.2 (E7)	
phenylbenzoate	+0.9 (ZLI-1052)	

[a] A negative value is obtained, of the order of magnitude of the numerical error (~0.1 Å^3).

electrostatic interactions.[17] The two solvents have indeed large and opposite dielectric anisotropies ($\epsilon_{\parallel} - \epsilon_{\perp} = -8.2$ for CCN55 and +10.3 for ZLI-1132, at 20 °C), due to the presence of a strong electric dipole roughly perpendicular to the alignment axis in one case, and parallel to it in the other.[4] The multisided role played by electrostatic interactions appears from the LXNMR analysis: on one hand they do not seem to influence the conformational distributions of MPS in ZLI-1132 and CCN55, but on the other hand they are decisive in governing the orientational order in the two solvents. More difficult to figure out is the origin of the different orientational behaviors of MPS in EBBA compared with those in the CN solvents, because of the more pronounced differences between the two kinds of solvents. Besides electrostatics (EBBA has a small negative dielectric anisotropy, deriving form the presence of a relatively small dipole moment, roughly perpendicular to the long molecular axis), also structural features should be taken into account: aromatic−aromatic interactions and steric repulsions involving the broad, flat, rigid core of EBBA are expected to play a significant role.

With reference to the phenomenon of chiral induction, which is the main object of our investigation, it is worth recalling that the axis of the cholesteric helix is perpendicular to the local director, and the solute tends to align to what we have denoted as the *b* axis. Considering now the three framed structures in Figure 5, which correspond to high probability geometries in the three solvents, we can see that the average molecular orientation with respect to the helix axis is quite different in the three cases. This result alone is not sufficient to predict the twisting ability of MPS in the three solvents, but at least it suggests that different helicities might be transferred to the medium in the three cases.

2.2. HTP Measurements and Predictions of the Surface Chirality Method. Helical twisting power of the (*S*)-MPS enantiomer has been measured in various solvents. The HTP values are reported in Table 2. In all cases a small HTP is found, with a sign which depends on the solvent. As for other flexible alkyl aryl sulfoxides,[7] opposite handedness is found in $CN_{\parallel}$ solvents (ZLI-2395, ZLI-1083, ZLI-1132, and E7) and phenylbenzoates or benzylideneanilines. Moreover, opposite handedness is also measured in $CN_{\parallel}$ and $CN_{\perp}$ solvents.

As we have seen above, differences in orientational order and conformational distribution of MPS in the three classes of solvents have emerged from the NMR analysis. However, due to the complexity of the mechanism of cholesteric induction, the relation among HTP, orientational order, and conformational distribution is not straightforward. To establish this link, calculations based on the surface chirality method [5] have been performed. According to this model the helical twisting power can be expressed as

$$\beta = (RT\xi/2\pi K_{22}v_m)Q \tag{3}$$

where R is the gas constant, T is temperature, while K_{22} and v_m are the twist elastic constant and molar volume of the solution, which for high dilution practically coincide with those of the solvent. The parameter ξ represents the orienting strength of the liquid crystal environment, and Q is the chirality parameter, which depends on the coupling of chirality and orientational behavior of the dopant. It is defined as

$$Q = -\sqrt{(^2/_3)}\,(Q_{aa}\,S_{aa} + Q_{bb}\,S_{bb} + Q_{cc}\,S_{cc}) \tag{4}$$

where $S_{\zeta\zeta}$ are principal elements of the Saupe ordering matrix **S**, and $Q_{\zeta\zeta}$ are the corresponding components of the helicity tensor ***Q***. This describes the helicity of the molecular surface and accounts for the chirality of intermolecular interactions. The component $Q_{\zeta\zeta}$ describes the helicity of the molecular surface of the dopant as viewed along the ζ axis. As a matter of fact, contributions of different sign and magnitude to HTP can derive from different regions in the molecule.[18] The ***Q*** tensor depends on the molecular conformation; therefore also the chirality parameter is a function of the torsional angle, $Q = Q(\phi)$. The measured helical twisting power is proportional to $\bar{Q}$, which is defined as the average over the torsional angle, weighted by the probability distribution $p(\phi)$:

$$\bar{Q} = \int Q(\phi)\,p(\phi)\,d\phi \tag{5}$$

Given the geometry of the dopant, the molecular surface is defined and the chirality tensor ***Q*** can be calculated; this is a function of the molecular shape, then of the torsional angle.

The chirality parameter $Q(\phi)$ has been calculated for each conformation according to eq 4, by using for each solvent the principal order parameters $S_{\zeta\zeta}(\phi)$ obtained by LXNMR, together with the corresponding components of the chirality tensor, $Q_{\zeta\zeta}(\phi)$, evaluated on the basis of the molecular surface. It is worth pointing out that the tensor components Q_{cc}, Q_{bb}, and Q_{aa} can be significantly different for the three solvents since, as we have seen, the orientation of the *a*,*b*,*c* axes change with solvent. It follows that, due to the different orientation, the solute in a given conformation is expected to have different twisting abilities in the three solvents.

The $Q(\phi)$ profiles calculated according to eq 4 for ZLI-1132, CCN55, and EBBA are shown in Figure 6. In the same plots also the torsional angle distributions from LXNMR are shown, to highlight the range of ϕ values which give the strongest contribution to the average chirality parameter $\bar{Q}$, according to eq 5. The importance of a change of alignment axes and order parameters appears from comparison of the $Q(\phi)$ profiles. Those obtained in CCN55 and ZLI-1132 look quite different; in particular we can see that the stable conformations of MPS, which correspond to the same geometry in these two solvents, are characterized by negative values of the chirality parameter

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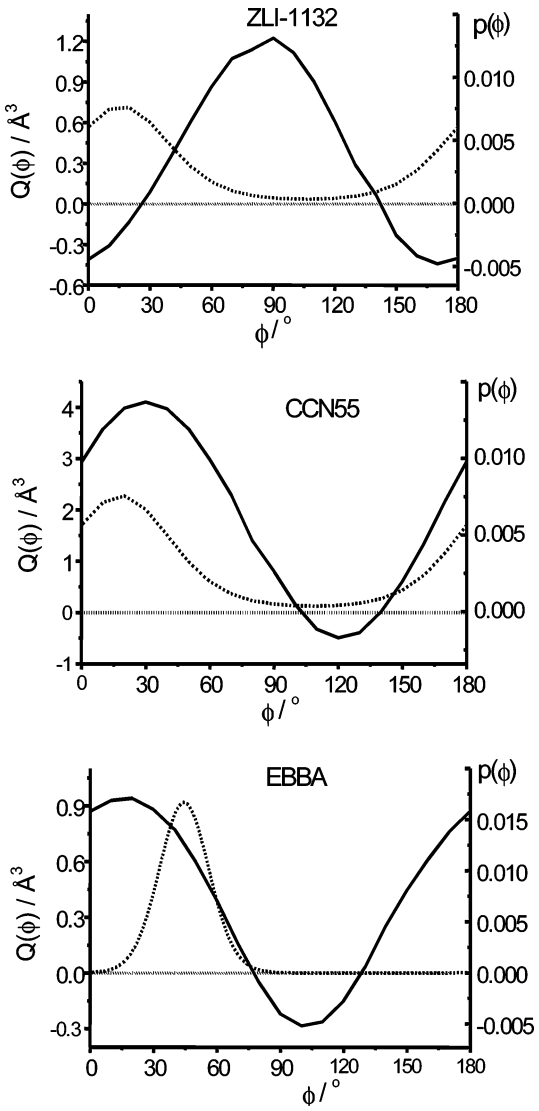

Figure 6. Dependence on the torsional angle ϕ of the chirality parameter Q calculated as explained in the text for the nematic solvents ZLI-1132, CCN55, and EBBA (solid lines). Dotted lines represent the probability distribution for the OS−CC dihedral angle, $p(\phi)$.

in ZLI-1132, whereas positive values are predicted in CCN55. This result is in agreement with the sign of the helical twisting observed in the two solvents, and the origin of the behavior can be explained by the different alignment of MPS. If we compare the framed configurations in Figure 5, we can see that the molecule, viewed along the axis of the cholesteric helix, looks different in ZLI-1132 and in CCN55. The $Q(\phi)$ profile obtained for MPS in EBBA is different from both those obtained in the other solvents. The angular dependence of Q is roughly the opposite of that in ZLI-1132 (with maxima in EBBA roughly corresponding to minima in ZLI-1132, and vice versa); the profile looks more similar to the angular dependence in CCN55, but with smaller values altogether. In the case of EBBA also a different conformational distribution has to be taken into account. However even in this case a major role is played by the orientational behavior: we can see in Figure 5 that the dopant orientation in EBBA is different, in different respects, from both those in ZLI-1132 an in CCN55. A positive HTP is predicted for the stable conformations of MPS in EBBA, again in agreeement with experiment.

The $\bar{Q}$ values in the three solvents, calculated with eq 5 by averaging over the conformational distribution, are reported in Table 2. According to eq 3 the $\bar{Q}$ value is proportional to the helical twisting power, with a proportionality factor which depends on solvent. By using reasonable values ($T \sim 300$ K, $K_{22} \sim 3 \times 10^{-12}$ N, $v_m \sim 3 \times 10^{-4}$ m^3, $\xi \sim 3 \times 10^{-2}$ Å^{-2}) we obtain β [μm^{-1}]/Q [Å^3] $\approx$ order of the unity. We can see that the predicted values have the correct order of magnitude and, more important, they show a clear trend with solvent, going from negative to positive on moving from $CN_{||}$ to $CN_{\perp}$ through EBBA, in agreement with experiment. The change in sign more clearly appears from comparison of the Q values for the stable conformations in Figure 6. A closer comparison between calculated and measured quantities is made difficult by a number of reasons. First of all, the surface chirality method is based on a simple parametrization of the chirality of intermolecular interactions. In addition, the unavoidable uncertainty in torsional angle distribution $p(\phi)$ and order parameters $S_{\zeta\zeta}$ entering eqs 4 and 5, especially in correspondence of the less stable conformations, can affect the calculated $\bar{Q}$ values. Finally, precise estimates of the parameters entering eq 3 are not available, especially for the commercial mixtures. Therefore accurate predictions of helical twisting power, a property resulting from the fine balance of contributions, cannot be expected. Nevertheless, unambiguous results have been obtained, which allow us to explain the experimental findings.

3. Conclusion

Cholesteric induction originates from the interplay of the anisotropy and chirality of the interactions experienced by the chiral dopant in the liquid crystal phase. If the dopant is a flexible molecule, the solvent influences the observed HTP in different interlinked ways, which cannot be easily disentangled. On one side solvent affects the torsional potential and the conformational distribution, so the chirality of the structures present in the solution. On the other side, it is responsible for orientational order, which is essential for the emergence of the phase chirality. In this work we have considered the chiral dopant methyl phenyl sulfoxide in different solvents, which can be grouped into three classes: weakly polar solvents with broad aromatic cores (phenylbenzoates and benzylideneanilines) and more polar and flexible solvents, with the electric dipole either longitudinal or transversal (cyanobicyclohexyls and cyanophenylcyclohexyls). We have seen that MPS has low twisting ability, and the cholesteric phase induced by the (*S*) enantiomer is left-handed in cyanobicyclohexyls and cyanophenylcyclohexyls solvents with longitudinal dipole, and right-handed in the other cases.

With the help of a molecular theory it has been possible to use the results of the LXNMR analysis, from which conformational distribution and orientational order of the dopant can be obtained, to make predictions of HTP in the three classes of solvents. In this way a detailed description of the phenomenon is obtained; a complex picture emerges from the analysis, wherein the multiform role played by solvent appears. In the following, the results of our investigation will be summarized, without neglecting a number of unexplained issues which stimulate future work.

(i) The conformational distribution of MPS is very similar in cyanobicyclohexyl and cyanophenylcyclohexyl solvents,

irrespective of the orientation of the dipole in the solvent molecule, whereas significant changes are observed in solvents with a broader aromatic core and a lower value of the average dielectric permittivity, like phenylbenzoates and benzylideneanilines. The results obtained suggest that packing effects, determined by short-range steric interactions which strongly depend on the structure of solute and solvent, might be important in determining the stability of MPS conformations. Further work is needed to gain a deeper insight into this aspect, which goes beyond the main aim of the present work.

(ii) The orientational order of MPS is different in the three classes of solvents and appears to depend on both electrostatic and structural properties of solvent. Not only the degree of order but also the alignment axes of the solute change with solvent. This kind of behavior has already been observed for other small solutes in nematic solvents,[16] and the molecular mechanism behind it is not fully clear yet.

(iii) As the main result of this work, we have shown that the change of cholesteric handedness with solvent is substantially driven by a change in orientation of the dopant. Namely, this is the only reason for the cholesteric helix inversion on going from ZLI-1132 to CCN55. In the case of EBBA also a variation in the conformational distribution has to be considered, but again the different alignment is the main reason for the change of handedness with respect to ZLI-1132. The orientational differences in the three solvents, illustrated in Figure 5, might appear not very significant; indeed, the system under investigation gives an example of a peculiar feature of chiral properties, i.e., the dramatic effects of even small variations at the molecular level.

By a proper combination of experiments and theory, we have been able to identify the subtle differences in solute−solvent interactions which underlie the puzzling behavior of the chiral solute MPS in nematic solvents. A given enantiomer can potentially induce left- and right-handed chiral nematic phases; the actual handedness is selected by solvent, mainly through its orienting peculiarities, even though effects on the conformational distribution can also play some role. This is a general rule, which holds for all chiral dopants; however changes in alignment and conformational stability with solvent are much weaker in the case of bulky molecules, with clear orientational preferences, which can only be slightly modified by the structural features of the solvent.

4. Experimental Section

4.1. Synthesis. (*S*)-Methyl phenyl sulfoxide has been prepared according to the procedure described in ref 19. Racemic methyl phenyl sulfoxide-α-^{13}C (MPS-13C) has been obtained via oxidation of thioanisole-α-^{13}C according to the following procedure.

Thioanisole-α-^{13}C: Thiophenol (1.32 g, 12.0 mmol) was allowed to react with sodium methoxide (16.0 mmol) in dry methanol (40 mL) at −10 °C. The reaction mixture was stirred and cooled for an additional 10 min, and 2.00 g (14.0 mmol) of iodomethane-^{13}C were slowly added. After stirring for 1 h at room temperature and removal of the solvent at reduced pressure, the residue was hydrolyzed with water (100 mL) and the aqueous phase was extracted with ether (4 × 70 mL). All the organic phases were combined, dried (Na_2SO_4), and freed of the solvent at reduced pressure to afford the thioanisole-α-^{13}C as a liquid which was further purified by column chromatography with Merck 60 silica gel (70−230 mesh) and with hexane as eluent. The obtained thioanisole-α-^{13}C weighed 1.11 g (8.9 mmol) (74%). MS (*m*/*z*): 125 (100% M^+), 109 (38%), 92 (30%), 78 (32%).

Methyl Phenyl Sulfoxide-α-^{13}C: A solution of metaperiodate (1.44 g, 6.7 mmol) in 10 mL of bidistilled cooled water to 0 °C was added to thioanisole-α-^{13}C (0.80 g, 6.4 mmol) and allowed to react for 3 h. Then the reaction mixture was submitted to the following treatments: addition of bidistilled water (10 mL), extraction with chloroform, anhydrification with Na_2SO_4, evaporation of the solvent, and column chromatography with Merck 60 silica gel (70−230 mesh) and with hexanes−ethyl acetate (40:60) as eluent. The solid methyl phenyl sulfoxide-α-^{13}C weighed 0.86 g (6.1 mmol) (95%). MS (*m*/*z*): 141 (1% $M^+ + 1$), 140 (91%), 125 (100%), 109 (11%), 97 (47%), 91 (11%), 77 (50%).

4.2. Helical Twisting Powers. Cholesteric pitches and handedness were obtained at room temperature using the lens version of the Granjean−Cano method.[20]

4.3. NMR Experiments. LXNMR experiments were performed by using the racemic mixture of MPS-13C. Samples were prepared by dissolving approximately 10 wt % of MPS-13C in the nematic solvents ZLI1132, EBBA, and CCN55 (all purchased from Merck Ltd.). The ^{13}C- and ^{1}H-LXNMR spectra were recorded at 298 K (a) on a Bruker AC 300, working at 7.04 T (MPS-13C in ZLI-1132 and CCN5) and (b) on a Bruker AVANCE 500 working at 11.7 T (MPS-13C in EBBA) on samples contained in 5 mm o.d. sample tubes. The free induction decays were stored in 32 kWords of computer memory giving a Hz/pt precision ratio on measuring the peak position of 0.49, 0.21, and 0.25, respectively, in ZLI1132, EBBA, and CCN55.

4.5. Surface Chirality Calculations. According to eq 4, evaluation of the chirality parameter $Q(\phi)$ for a given molecular geometry requires the chirality tensor $\boldsymbol{Q}$ and the ordering matrix **S**. The elements of the chirality tensor, which depend on the chirality of the molecular surface, are calculated in the following way.[5] Given the nuclear positions for a specified value of the torsional angle ϕ, the molecular surface is generated. This is defined as the surface drawn by the center of a bead rolling on the assembly of interlocking van der Waals spheres centered on the nuclei and is approximated by a set of triangles, obtained with the algorithm developed by Sanner et al.[21] The following radii have been assumed for calculating the surface of MPS: $r_{CH(aromatic)} = 2$ Å, $r_{C(methyl)} = 1.85$ Å, $r_{H(methyl)} = 1.2$ Å, $r_S = 2$ Å, $r_O = 1.5$ Å. The geometric parameters are specified in Table A2 of App. − s. A3 − in the SI; the same values have been used for the analysis of NMR data and for the calculation of the tensor $\boldsymbol{Q}(\phi)$. For the elements of the Saupe matrix appearing in eq 4, the values derived from the NMR analysis were used for each solvent.

Acknowledgment. The paper is dedicated to Professor Giovanni Gottarelli, author of seminal works on cholesteric induction, on the occasion of his 65th birthday. This work has been supported by MIUR (PRIN2003 "Cristalli Liquidi e Macromolecole per Nanostrutture Organizzate"). A.F. acknowledges additional support from FIRB2001 (RBNE01P4JF). F.I. acknowledges support from Unical University Funds. The authors gratefully acknowledge Prof. M. Longeri (LXNMR, S.C.An. Lab., Dipartimento di Chimica, Università della Calabria) for stimulating discussions and Professor Carlo Rosini (Università della Basilicata) for supplying enantiopure MPS.

Supporting Information Available: Appendix containing details about the following: (A1) Analysis of NMR Spectra; (A2) Theoretical Background; (A3) Geometries of Rigid Subunits; (A4) Conformational and Orientational Analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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