Determination of absolute configuration of helicenes and related biaryls from calculation of helical twisting powers by the surface chirality model

Alberta Ferrarini,[a] Giovanni Gottarelli,[b] Pier Luigi Nordio †[a] and Gian Piero Spada[b]

[a] Dipartimento di Chimica Fisica "A. Miolati", Università di Padova, Via Loredan 2, 35131 Padova, Italy
[b] Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, Via S. Donato 15, 40127 Bologna, Italy

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The sign and the magnitude of the helical twisting power β for a series of helicenes have been calculated by the Surface Chirality model. The principal contribution to β derives from the helicity in the direction perpendicular to what can be defined as the main molecular plane; the cholesteric axis is also predicted to be along this direction, in agreement with a view of the cholesteric induction by helical molecules based on empirical observations. In the case of non-rigid biphenanthryl derivatives, the value of β is predicted to vary with the dihedral angle between the phenanthryl moieties, changing sign at about 90° where the conformation passes from s-*cis* to s-*trans*, *i.e.* when the stereochemical descriptor of the biaryl moiety exchanges the *M* and *P* indices. Comparison between experimental and calculated values indicates an s-*trans* conformation for the flexible dopants, in agreement with a previous conclusion drawn from empirical correlations. The Surface Chirality model appears to be a promising technique to assess the absolute configuration of rigid molecules by the comparison of experimental and calculated β values. For flexible molecules, the quality of the information depends critically on the degree of knowledge of their conformational freedom.

Introduction

Chiral resolved molecules are usually characterised by measuring their optical rotation, in general referred to the sodium D-line, or their circular dichroism spectra. Both methods are essentially spectroscopic and involve interaction of the electromagnetic radiation with the electrons of the molecules.

An alternative non-spectroscopic way of characterising chiral molecules is the measurement of their twisting power in nematic liquid crystals.[1,2] It is known that the addition of traces of a chiral solute to an achiral nematic liquid crystal induces the formation of a helical cholesteric structure, characterised by its handedness and pitch. Equal amounts of enantiomeric solutes induce helical structures with identical pitch and opposite handedness. Different substances show different abilities to twist the nematic phase, the helical twisting power being defined by eqn. (1),[3] where p is the pitch (in micrometers), c the concentration (moles of solute per mole of solvent) and r the enantiomeric purity of the dopant. The signs + or − indicate right-handed and left-handed cholesteric helices, respectively. The value of β is constant in a large range of concentrations and changes with the nature of the solvent. The twisting power can therefore characterise a chiral molecule in a similar way to optical rotation; as β is a non-spectroscopic quantity, it is expected to give different and hopefully complementary stereochemical information.[4–8]

$$\beta = (p\ c\ r)^{-1} \qquad (1)$$

The measurements of pitch and handedness are simple and require only a common microscope with polarizers and a graduated scale in the ocular or an $x - y$ translator.[9–11] Furthermore, the quantity of resolved compound needed is much smaller than for optical rotation.

A quantitative relation between the twisting power and the molecular structure of the chiral dopant is derived by a theoretical method known as the Surface Chirality model. This is a model which, without dealing with the origin of the intermolecular forces, accounts in a phenomenological way for the short-range interactions of the solute molecule with the surrounding solvent, which are modulated by the solute molecular shape. Despite some approximations inherent in the derivation of the model[12–14] and the obvious difficulties in its application to molecules with many degrees of internal freedom, the method has been successfully employed to calculate β values for systems of various complexities, such as substituted biaryls and heptalenes.[13,15,16]

In this paper we show that it is possible to predict correctly the sign and magnitude of the twisting power for a group of helical-like molecules with rigid geometry [(*M*)-**1**–**4**]. We have extended the investigation to analogous but conformationally flexible derivatives [(*R*)-**5**–**8**], and also in these cases, calculations of β for conformers predicted as the most stable are in agreement with experimental observation. This result confirms that for systems with internal flexibility the method can be applied with confidence to deduce information on the preferred conformations.

Results and discussion

The absolute configuration of helicenes

Helicenes are characterised by a helical structure made up of *ortho*-condensed aromatic rings,[17,18] the helical structure being a consequence of the steric interaction between terminal aromatic nuclei. The synthesis of the first optically active helicene (hexahelicene, **1**) was reported by Newman[19] in 1956 and a number of heterohelicenes, especially those containing thio-

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† Pier Luigi Nordio died on the 20th of October, 1998. His human and scientific presence will always be with us.

phene units,[20] was subsequently described. The assignment of the absolute configuration of helicenes has mainly followed three distinct lines of approach: X-ray diffraction studies using Bijvoet's method, chemical correlation, and calculations based on chiroptical properties. The absolute configuration of (−)-hexahelicene **1** has been unambiguously determined as (*M*) by a Bijvoet X-ray structure determination of the (−)-2-bromo derivative which was then chemically converted to the (−)-hexahelicene.[21] This assignment is in agreement with the best available calculations,[22,23] though not with the earlier ones performed by less refined methodology,[24] and was finally confirmed by chemical correlation.[25,26] The configuration of tetrahelicene **2** was deduced by SCF calculations.[27]

The configuration of the helicene-like compound **4** was determined by chemical correlation[28] with the precursor 4,4′-biphenanthrene-3,3′-diol whose configuration was already established.[29,30] The configuration of heterohelicene **3** was deduced from chemical correlation[28] with the same biphenanthrenediol. This assignment is in agreement with what is expected from resolution with TAPA[28,31,32] [2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylideneaminooxy)propionic acid] and from qualitative comparison of its CD spectrum[33] with those of a series of heterohelicenes[34] whose absolute configurations were unambiguously assigned. The analogy of CD spectra[34] of heterohelicenes containing thiophene moieties in different positions and the behavior of the latter when treated with TAPA resolving agent[31,32] allow one to extend the configurational assignment to different helicenes if the absolute configuration of one of them is known. The configuration of a hetero[6]helicene containing a benzodithiophene unit was assigned by X-ray diffraction[20] and confirmed by chemical correlation[25] and SCF calculation of the optical activity.[20,34]

The absolute configuration of **5**–**8** was determined by chemical correlation[28] with the precursor 4,4′-biphenanthrene-3,3′-diol, whose configuration has been unambiguously established.[29,30]

Although the absolute configurations of the helicenes investigated have been already obtained, the methods used are not of general application and suffer some limitations: X-ray diffraction requires the availability of crystals of appropriate characteristics, chemical correlation requires the existence of a stereocontrolled pathway, and empirical comparison of CD spectra is severely dependent on the nature of the chromophoric part of the molecule. In addition, calculations of the chiroptical properties cannot always be considered fully reliable. Despite initial difficulties in the calculation of the optical rotation of simple molecules,[35,36] recently, substantial progress in this area has allowed the determination of absolute configuration of complex molecules.[37]

In the present paper, we show that it is possible to predict the helical twisting power of helicenes and related molecules and hence to determine their absolute configuration. The method presented here, based on the surface interaction between solvent molecules and a chiral probe, is independent of the solute electronic properties which determine the chiroptical behaviour.

The surface chirality model

The theoretical model has been presented in detail elsewhere,[13,14] and only the main physical aspects of the mathematical problem will be reviewed here. The model is based on the assumption that solely the molecular shape of a solute determines its alignment in the local nematic environment, and that the twisted shape of the chiral probe is able to exert a torque on the local nematic director, this effect being transmitted at a distance of thousands of molecular lengths by virtue of the elastic properties of the nematic medium.[14]

Implementation of the model requires a mathematical description of the molecular shape, and a statistical mechanics treatment for the distortion free energy. This treatment is reminiscent of that presented in the de Gennes book to consider the competing effect of wall alignment and field-alignment, for the case of pure twist.[38]

The molecular surface is constructed by considering the molecule as an assembly of van der Waals spheres centred at the atomic positions.‡ By exploring the molecular surface by unit vectors normal to each surface element, numerical values for two molecular properties, termed as "surface" $\boldsymbol{T}$ and "helicity" $\boldsymbol{Q}$ tensors respectively, are obtained.[41] The tensors are defined in any arbitrary molecule-fixed axis system, but it is always possible to identify for each of them a principal axis system in which the tensor has only diagonal elements, called principal values. In general, the surface and helicity tensors have different principal axes, unless rotational symmetry axes do exist, which, in this case, are principal axes for both tensors.[42]

The values (T_{xx}, T_{yy}, T_{zz}) of the surface tensor define the tendency of the corresponding molecular axes to align along the nematic director; the values (Q_{xx}, Q_{yy}, Q_{zz}) of the helicity tensor quantify the helicities as viewed along those axes. According to common convention, a positive (negative) Q_{ii} value indicates right (left)-handed helicity of the molecular surface along the *i*-th molecular axis. Both tensors are traceless, *i.e.* the sum of their diagonal elements is equal to zero. It is important to recall the different mathematical properties of the surface and helicity tensors. The surface tensor is a second-rank tensor like the polarizability or inertia tensor, while the helicity tensor is a pseudo-tensor, whose components vanish for molecules having improper rotations as symmetry operations, with the exception of molecules belonging to non-enantiomorphous groups such as C_h, C_{2v}, D_{2d} and S_4.[42,43]

A well-known property mathematically related to the surface tensor is the molecular ordering matrix $\boldsymbol{S}$,[44] generally determined by magnetic resonance experiments. The ordering matrix is also traceless, and its principal axes coincide with those of the surface tensor. The elements S_{ii} have values ranging between $-\frac{1}{2}$ and 1, a positive value denoting the tendency of the *i*-th molecular axis to align with the director, and a negative value the tendency to be aligned perpendicular to the director. The magnitude of S_{ii} gives the degree of alignment of the *i*-th molecular axis; thus, the difference $S_{ii} - S_{jj}$ measures the different tendency to alignment of the *i*-th and the *j*-th axes.

Statistical methods allow one to derive an expression for the distortion free energy per unit volume of the sample, due to its elastic fluctuations and the twist deformation exerted by the chiral probe. Under the condition that the induced pitch is much larger than molecular dimensions, minimisation of the distortion free energy leads to the relation in eqn. (2) for the

$$\beta = RT\varepsilon Q/2\pi K_{22}v_m \qquad (2)$$

twisting power of a specific dopant in a given nematic solvent,[14] where T is the absolute temperature, and ε, K_{22} and v_m are respectively orienting strength, twist elastic constant and molar volume of the nematic solution (which for very low dopant concentrations are those of the solvent); the chirality order parameter Q is defined by eqn. (3), where x, y, z are the prin-

$$Q = -(2/3)^{1/2}(Q_{xx}S_{xx} + Q_{yy}S_{yy} + Q_{zz}S_{zz}) \qquad (3)$$

cipal axes of the ordering matrix $\boldsymbol{S}$ (and the surface tensor $\boldsymbol{T}$). Thus the twisting power is proportional to the chirality order parameter, which is essentially a molecular property with a proportionality factor which depends on measurable properties of

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‡ Other descriptions are possible, *e.g.* by defining the surface enclosing the electron density obtained by quantum mechanical calculations,[39] or by considering the smoothed surface generated by rolling a sphere over the van der Waals envelope.[40] However, in the present case, we have used the widely accepted molecular representation by van der Waals spheres, which has the advantage of being simple and has been used for a number of successful predictions.[13,15,16]

the solvent. It should be remembered that the orienting strength parameter ε at the temperature of the experiment can be derived from molecular order parameters in the nematic solvent.[45,46]

In the present case, the solvent is the nematic mixture E7 at $T = 300$ K, which corresponds to a reduced temperature $T/T_c \approx 0.9$. The proportionality factor between Q and β has been calculated using the values $K_{22} = 8 \times 10^{-12}$ newton and $v_m = 3 \times 10^{-4}$ m^3, reported in the literature.[47] In the absence of experimental data on the ordering matrix of our solutes, the parameter ε has been taken to be equal to 5 nm^{-2}. This choice is justified by the fact that such a value provides an order parameter approximately equal to 0.5 for the long molecular axis of elongated molecules of the dimensions of cyanobiphenyl mesogens,[13,45] at a reduced temperature of about 0.9. By using these solvent parameters, a value of about 1000 is predicted for the ratio β/Q, if the twisting power β is expressed in μm^{-1} units and the chirality order parameter Q in nm^3 units.

In order to gain some understanding of the results expected by the model, we shall consider as an example the case of a disc-like object, twisted along the (x,z) axes in the disc plane in such a way as to have the symmetry of a right-handed four-blade propeller. The y-axis is therefore the symmetry axis, and it is a principal axis for both the ordering matrix and the helicity tensor. Because of the axial symmetry and the traceless character of the tensors, the relations (4) and (5) must be obeyed, with (5)

$$S_{xx} = S_{zz} = -S_{yy}/2, \quad Q_{xx} = Q_{zz} = -Q_{yy}/2 \qquad (4)$$

$$Q = -(3/2)^{1/2} Q_{yy} S_{yy} \qquad (5)$$

following from (4). When dissolved in a nematic environment formed by elongated mesogens, the y-axis of the twisted disc will preferentially align perpendicular to the director, so that S_{yy} must be negative.

Since Q_{yy} is positive for a right-handed helical configuration of the probe, the chirality order parameter Q comes out to be positive, and the induced cholesteric helix is predicted to be right-handed according to eqn. (2).

Calculated and experimental helical twisting powers

Helicenes. The molecular structures were obtained by full geometry optimisation based on *ab initio* SCF-MO calculations at the 6-31G** level. The calculations were performed with the GAUSSIAN94 program package.[48] In all cases overall-twisted structures with skewed phenanthryl units were obtained. The calculated structures are in good agreement with those determined from X-ray diffraction for **1**[49] and other helicenes,[17,18,20,50] and the differences between chirality order parameters obtained with the two sets of structures do not differ more than 10%.

Given the molecular geometries, surface and helicity tensors were calculated on the basis of molecular surfaces defined as assemblies of van der Waals spheres centred at nuclear positions, in the united atom approximation. Table 1 reports for (*M*)-**1**–**4** the principal elements of the surface tensor ***T***, in addition to the diagonal elements of the helicity tensor ***Q*** in the principal axis system of the surface tensor and in its own principal frame. Furthermore, Table 1 shows the principal values of the orientational ordering matrix ***S*** and of the chirality order parameter Q multiplied by 1000, which is the factor β/Q calculated for the E7 solvent. In addition, experimental helical twisting powers are also reported.[33] We have labeled as x, y, z the principal axes of the surface tensor ***T***, coincident with the principal axes of the ordering matrix ***S*** (see Chart 1). In particular, we have taken as z and y the axes with the most pronounced tendency to stay along the director (corresponding to the largest positive ***T*** and ***S*** components) and perpendicular to it (largest negative ***T*** and ***S*** components), respectively. For the molecules under consideration the y axis is perpendicular to the approximate molecular plane. The x and z axes lie on this plane, with x parallel to the C_2 or *quasi*-C_2-axis. As seen in Table 1, the preferential alignment of the z axis is not very pronounced in the case of (*M*)-**1** and (*M*)-**3**, in contrast with the behaviour of

Table 1 Principal elements of the surface tensor ***T***, diagonal elements of the helicity tensor ***Q*** in the principal axis system of the surface tensor and in its principal frame, principal values of the ordering matrix ***S***, chirality order parameter Q calculated with $\varepsilon = 5$ nm^{-2} and experimental helical twisting powers β taken from ref. 33, for derivatives (*M*)-**1**–**4**

	(*M*)-**1**	(*M*)-**2**	(*M*)-**3**	(*M*)-**4**
T_{xx}/nm^2	0.27	0.16	0.32	0.20
T_{yy}/nm^2	−0.56	−0.46	−0.66	−0.53
T_{zz}/nm^2	0.29	0.30	0.34	0.33
Q_{xx}/nm^3	0.066	0.047	0.058	0.072
Q_{yy}/nm^3	−0.084	−0.043	−0.092	−0.074
Q_{zz}/nm^3	0.018	−0.004	0.034	0.002
Q_{aa}/nm^3	0.066	0.049	0.058	0.072
Q_{bb}/nm^3	−0.087	−0.052	−0.092	−0.089
Q_{cc}/nm^3	0.021	0.003	0.034	0.017
S_{xx}	0.16	0.03	0.18	0.06
S_{yy}	−0.35	−0.34	−0.38	−0.35
S_{zz}	0.19	0.31	0.20	0.29
1000 Q/nm^3	−36	−12	−43	−25
β/μm^{-1}	−55	−9	−20	−13

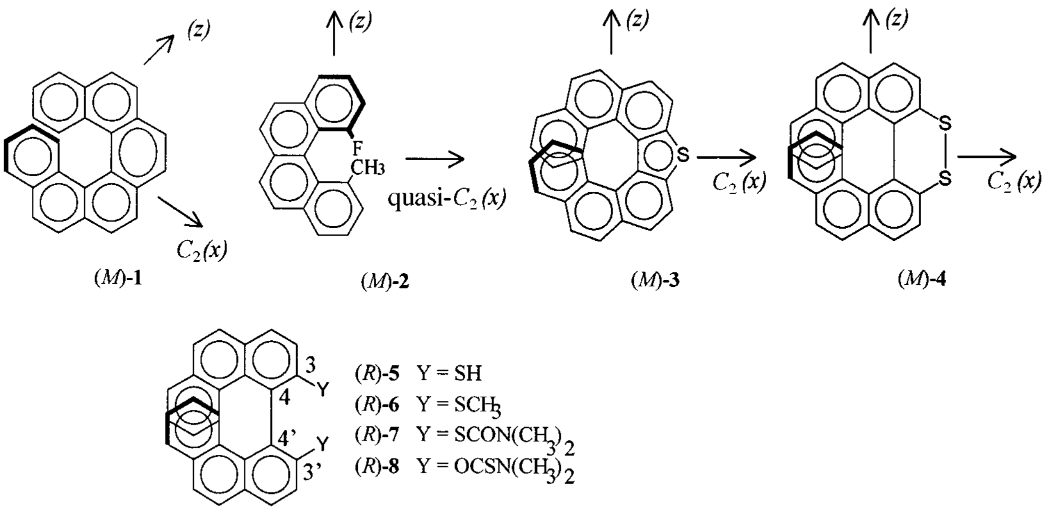

Chart 1 For the rigid compounds **1**–**4**, the approximate directions of the principal axes of the surface tensor are indicated.

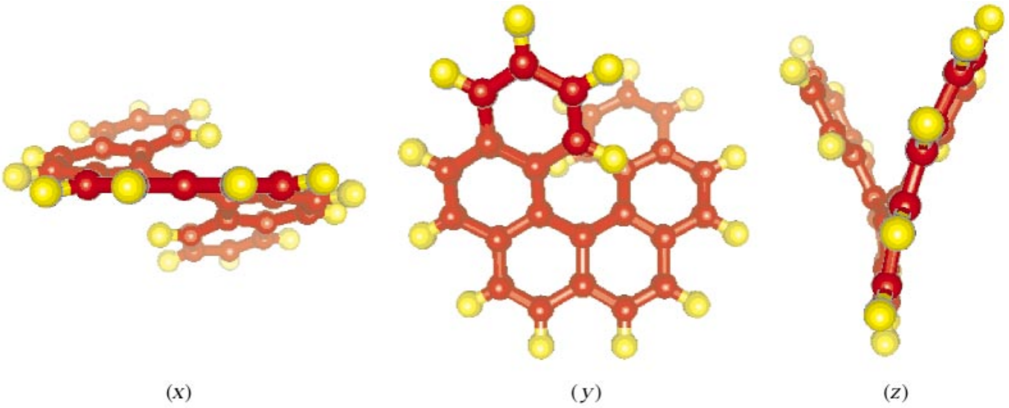

Fig. 1 Projections of (*M*)-**1** on the principal planes of the surface tensor. Under each projection the label of the axis perpendicular to the projection plane is reported. Along the *y* axis the molecule shows a left-handed screw-like structure (Q_{yy} negative).

(*M*)-**2** and (*M*)-**4**. In other words, the orientational behaviour of (*M*)-**1** and (*M*)-**3** is that of disc-like molecules, although the orientation with the C_2-axis perpendicular to the local director is slightly favoured. The molecules (*M*)-**2** and (*M*)-**4** are biaxial objects with little resemblance to discs or rods: they tend to stay with the director on the molecular plane, but in this plane there is a strongly preferred alignment axis, which for both molecules is perpendicular to the C_2 or quasi C_2-axis.

The principal axes of the helicity tensor $\boldsymbol{Q}$ are denoted as *a,b,c*, and in general do not coincide with the *x,y,z* axes unless they are determined by symmetry. Therefore, the two reference frames are expected to share only the C_2-axis in the molecules considered here. However, it results from calculations that the other principal axes of $\boldsymbol{Q}$ also lie very close to the corresponding principal axes of $\boldsymbol{T}$.

Fig. 1 shows, as an example, the projections of the molecular structure of (*M*)-**1** on the principal planes of the surface tensor $\boldsymbol{T}$. Table 1 shows that the four molecules are characterized by a negative helicity along the *y*-axis, while two positive values are predicted on this plane, one along an axis parallel to the C_2 or quasi C_2-axis, and the other along an axis perpendicular to it. The latter is in all cases the smallest in magnitude, in agreement with what has already been seen for model biphenyl and binaphthyl systems, where very low helicity is predicted along the bond connecting the two aromatic moieties.[12] In agreement with the stereochemical descriptor (*M*) established for the molecules considered here, a negative value of the helicity tensor component Q_{yy} is predicted. This means that a translation along the *y* direction of the molecular surface is associated with a left-handed rotation, as occurs for the translation of a left-handed helix in the direction of the helical axis (see Fig. 1, view along *y*). The sign convention agrees with that used to describe the configuration of rigid helical molecules (*P* or *M*). According to eqn. (4) a negative chirality order parameter *Q* is calculated, in keeping with experiment. The behaviour of these molecules can be summarised by saying that in the cholesteric phase the axis perpendicular to the molecular plane tends to align along the helix axis, producing twisted phases with the same handedness as the helicity along that axis.

The numerical values of *Q* agree, within a factor of the order 1000 as expected from solvent properties, with the experimental twisting powers. The discrepancies between theoretical and experimental values may be due to several factors: i) the uncertainty in the enantiomeric purity of the dopants; ii) the inadequacy of the geometries calculated for isolated molecules to represent actual structures in the liquid crystal environment; iii) the neglect of longer range interactions, involving electrostatic moments of the molecules, which can be more relevant in the presence of heteroatoms;[46] and iv) the simplified model for the solvent, treated as a continuum.

Open-chain derivatives. Encouraged by the successful estimates of twisting powers for rigid helicenes, we attempted the extension to the open-chain derivatives (*R*)-**5**–**8**. The result in these cases depends not only on the absolute configuration, but also on the twist angle *α* between the phenanthryl units and on the conformation of the substituents.

Let's take as an example (*R*)-**5**, which is the simplest of the open-chain derivatives considered here. Prediction of the twisting power would require the following procedure: (i) derivation of the torsional potential, (ii) calculation of the helicity tensor and order parameters, and hence of the chirality order parameter, for various torsional angles, and (iii) a (weighted) average of the *Q* values over the torsional angle distribution. The crucial point is the first step, which is computationally difficult, because accurate calculations are required to get torsional profiles and, even though the results may be reliable for isolated molecules, there are no reasons to believe that they are realistic when the molecules are dissolved in condensed phases. The procedure becomes even more complex for flexible molecules with several torsional angles, such as (*R*)-**6**–**8**. For this reason we did not perform, in the case of the open-chain derivatives, the complete analysis leading to *Q* values to be directly compared with experimental twisting powers. Instead, with the aim of getting some insight into the complex behaviour of these systems and of highlighting the sensitivity of the *Q* values towards the molecular conformation, we limited ourselves to the investigation of the stable conformers obtained by full geometry optimisation.

Ab initio calculations at the 6-31G** level were performed for the derivatives (*R*)-**5** and (*R*)-**6**, while the more complex structures of (*R*)-**7** and (*R*)-**8** were obtained by the semiempirical method PM3. Again the software package GAUSSIAN94 was used.[48] In all cases, with the only exception of one of the conformers of (*R*)-**8**, the energy minima corresponded to a geometry with the phenanthryl units approximately perpendicular to each other, and much less twisted than in the case of the rigid systems.

For the conformers of the open-chain derivatives Table 2 reports the principal values of the surface tensor $\boldsymbol{T}$ and the diagonal elements of the helicity tensor $\boldsymbol{Q}$ in the principal axis system of the surface tensor and in its principal frame. In addition, the principal values of the ordering matrix $\boldsymbol{S}$ and the chirality order parameter *Q* are shown in the table. As for helicenes, the reference axes are labelled in such a way that *z* and *y* correspond to the principal axes of $\boldsymbol{T}$, with the strongest tendency to being oriented parallel and perpendicular to the nematic director, respectively.

It can be seen from Table 2 that the various conformers have similar properties, with the only exception being the $\mathbf{A_2}$ conformer of (*R*)-**8**, which will be discussed in more detail in the following. It appears that, in contrast with the rigid systems considered above, the open-chain derivatives show a rod-like behaviour with a net tendency to align the axis lying close to the

Table 2 Principal values of the surface tensor ***T***, diagonal elements of the helicity tensor ***Q*** in the principal axis system of the surface tensor and in its principal frame, principal values of the ordering matrix ***S*** and chirality order parameter Q calculated with $\varepsilon = 5$ nm^{-2} for selected conformers of derivatives (*R*)-**5**–**8**. $\mathbf{A}_2$ and $\mathbf{A}_1$ refer to conformers with and without a C_2 symmetry axis perpendicular to the phenanthryl–phenanthryl bond. The experimental helical twisting powers β are taken from ref. 33

			(*R*)-**7**		(*R*)-**8**	
	(*R*)-**5**	(*R*)-**6**	$\mathbf{A}_2$	$\mathbf{A}_1$	$\mathbf{A}_2$	$\mathbf{A}_1$
T_{xx}/nm^2	−0.12	−0.09	0.9	−0.06	0	−0.08
T_{yy}/nm^2	−0.20	−0.20	−0.39	−0.28	−0.26	−0.28
T_{zz}/nm^2	0.32	0.29	0.30	0.34	0.26	0.36
Q_{xx}/nm^3	−0.151	−0.134	−0.213	−0.205	0.162	−0.188
Q_{yy}/nm^3	0.157	0.154	0.239	0.131	−0.021	0.193
Q_{zz}/nm^3	−0.006	−0.020	−0.026	0.074	−0.141	−0.005
Q_{aa}/nm^3	−0.156	−0.149	−0.218	−0.063	0.162	−0.190
Q_{bb}/nm^3	0.158	0.154	0.239	0.060	0.046	0.203
Q_{cc}/nm^3	−0.002	−0.005	−0.021	0.003	−0.208	−0.013
S_{xx}	−0.16	−0.12	0.17	−0.09	−0.04	−0.12
S_{yy}	−0.27	−0.27	−0.51	−0.36	−0.37	−0.35
S_{zz}	0.43	0.39	0.34	0.45	0.33	0.47
1000 Q/nm^3	9	17	62	4	45	18
β/μm^{-1}	8	28	7.5		16	

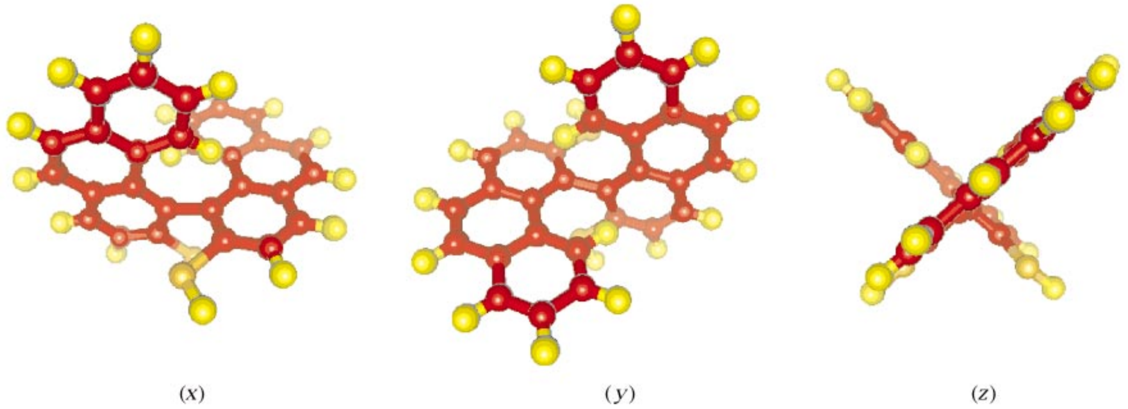

Fig. 2 Projections of (*R*)-**5** on the principal planes of the surface tensor. Under each projection the label of the axis perpendicular to the projection plane is reported. Along the y axis the molecule shows a right-handed screw-like structure (Q_{yy} positive).

phenanthryl–phenanthryl bond, which is therefore denoted as z axis, parallel to the director. The axis with the strongest tendency to orient perpendicular to the director (y axis) is for these systems the C_2 or quasi-C_2 axis. It can also be seen that, in analogy with the rigid compounds, the helicity along the axis parallel to the C_2 axis is large and positive and that along the axis perpendicular to both the C_2 and the phenanthryl–phenanthryl bond is large and negative. On the contrary, the helicity along the latter bond, which is much smaller in magnitude, changes its sign from positive to negative on passing from the rigid to the flexible systems, as expected in keeping with the change of the conformation from s-*cis* to s-*trans*. This dependence of the elements of the ***Q*** tensor on the dihedral angle characterising structures with axial chirality is rather general, and has been predicted also for biphenyl and binaphthyl, as well as for model systems.[13,14]

The simpler of the flexible derivatives is (*R*)-**5**, this stable conformer is predicted to have a twist angle $\alpha = 90.4°$ (hereafter α will be defined as the 3–4–4′–3′ dihedral angle). The general considerations made above appear in a clear way from the comparison of the molecules (*R*)-**5**, whose projections on the principal planes of the surface tensor are shown in Fig. 2, and (*M*)-**4**, which is very similar, but is forced by the S–S bond to reduce the angle between the phenanthryl moieties to about 53°.

In order to show the angular dependence of the chirality order parameter Q for (*R*)-**5**, we have considered a number of conformers generated from the minimum energy structure by changing the torsional angle α in a restricted range about 90.4°. As shown in Fig. 3, a significant dependence of the chirality order parameter appears, with sign inversion in the proximity of the perpendicular arrangement of the aromatic units. Analogous behaviour of the chirality order parameter as a function of the twist angle has been predicted for biphenyl and binaphthyl.[13]

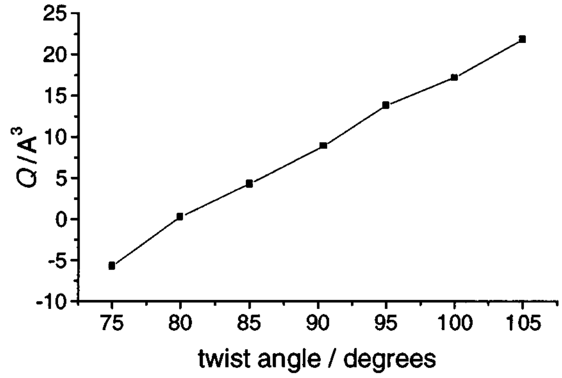

Fig. 3 Twist angle dependence of the chirality order parameter for (*R*)-**5**, calculated with $\varepsilon = 5$ nm^{-2}.

In the case of (*R*)-**6**, the lowest energy conformer has a twist angle $\alpha = 90.6°$ between the phenanthryl units (and C_{ring}–C_{ring}–S–CH_3 dihedral angles of about 180°). The projections of the molecule on the principal planes of the ***T*** and ***Q*** tensors are similar to those of (*R*)-**5**. As can be seen from the values reported in Table 2, the methyl substituents have the effect of increasing the chirality order parameter with respect to (*R*)-**5**.

The presence of longer substituents makes the analysis even more complex in the case of (*R*)-**7** and (*R*)-**8**. The lateral chains give a substantial contribution to the molecular chirality, which can substantially enhance or reduce that of the biphenanthryl skeleton, depending on their conformation. For each molecule geometry optimization was performed with and without C_2 symmetry constraint. In the case of (*R*)-**7** the more symmetric conformer ($\mathbf{A}_2$) has $\alpha = 92.9^\circ$ (and $C_{ring}–C_{ring}–S–CO = 123^\circ$), while the structure lacking any symmetry ($\mathbf{A}_1$) has $\alpha = 94.5^\circ$ (and $C_{ring}–C_{ring}–S–CO$ dihedral angles equal to 123° and −127°). The exchange of oxygen and sulfur leads to conformers for (*R*)-**8** quite different from those obtained for (*R*)-**7**, with a CS bond longer than the CO bond and the CSC bond angle smaller (106°) than COC (120°). The lowest energy conformers of (*R*)-**8** have $\alpha = 74.7^\circ$ (and $C_{ring}–C_{ring}–O–CS = 126.5^\circ$) for $\mathbf{A}_2$ conformer and $\alpha = 95^\circ$ (and $C_{ring}–C_{ring}–O-CS$ equal to 151° and −113°) for the $\mathbf{A}_1$ conformer. Significant differences in both orientational and chiral properties between the two conformers of each molecule appear from Table 2. The properties of the $\mathbf{A}_1$ conformers and those of the $\mathbf{A}_2$ conformer of (*R*)-**7** are analogous to those of (*R*)-**5** and (*R*)-**6**. For the $\mathbf{A}_2$ conformer of (*R*)-**8** the conformation passes from s-*trans* to s-*cis*, and correspondingly the helicity tensor component along the phenanthryl–phenanthryl bond becomes positive. The structure of this conformer is also reflected by its orienting behaviour, which is different from that of both the other open-chain s-*trans* conformers and the (s-*cis*) rigid helicenes: the directions of highest and lowest alignment are respectively the phenanthryl–phenanthryl bond and the normal to the plane containing this bond and the $\mathbf{A}_2$ axis. Finally, it can be seen from Table 2 that the chirality order parameters predicted for the $\mathbf{A}_2$ structures are high in magnitude and positive in sign even in the case of (*R*)-**8,** in spite of its s-*cis* conformation. This shows how, in the presence of bulky substituents, the twisting power cannot be simply related to the configuration of the biaryl moiety.

Conclusions

From the comparison between the results of the theoretical calculations and the stereochemical data for the series of helicenes analysed here, a number of significant conclusions can be drawn.

First, in all cases the correct handedness of the induced helical macrostructures is predicted unambiguously by the model. In particular, it turns out to be left-handed for the rigid chiral probes (*M*)-**1**–**4**, but it becomes right-handed for the open-chain systems (*R*)-**5**–**8**, where internal flexibility allows the molecules to adopt a s-*trans* conformation, with the phenanthryl rings at an angle slightly higher than 90°. In other words, Q changes sign when the conformation passes from s-*cis* to s-*trans*, and the stereochemical descriptor of the biaryl moiety changes from *M* to *P*.

Secondly, the chirality order parameter Q reproduces quite well, apart from a constant factor which depends on the solvent, the numerical values of the experimental twisting powers. To fully appreciate this result, it should be recalled that the computations are performed on molecular structures represented by van der Waals spheres of standard radii, with no adjustable parameters. The surface chirality model appears therefore a promising technique to assess the absolute configuration of rigid molecules. In the case of flexible systems, such as the (*R*)-**6**–**8** derivatives, the numerical values calculated for the twisting power depend rather critically on the molecular conformations. In principle it is possible to perform statistical averages over all metastable conformers, but this may be prevented in practice by the difficulty of obtaining the full multidimensional internal potential surface of the molecules. Further complications arise when the barriers separating the conformational sites are too low, because the quantum-mechanical calculations may not converge to a well-defined geometry.

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