On the assessment of molecular chirality

Alberta Ferrarini and Pier Luigi Nordio

Department of Physical Chemistry, University of Padova, 2 via Loredan, 35131 Padova, Italy

A property termed helicity tensor, defined on the basis of the molecular shape, is proposed to quantify the chirality of arbitrary molecules. Numerical implementation of the model can be easily done, once the molecular geometry is known. The principal components of the tensor represent helicities of the molecular surface as viewed along the three perpendicular axes. Results are presented for a number of systems, going from asymmetrically substituted methane derivatives to complex helicoidal structures. Although originally derived to predict the twisting power of chiral probes dissolved in liquid crystal solvents, the concept of helicity tensor provides a useful tool for many applications of molecular engineering.

Introduction

The concept of chirality is of utmost relevance in chemistry, and interest in the field has been renewed by studies in liquid crystal phases,[1] which have provided unique opportunities for investigating a variety of chiral solutes, opening the road to fascinating technological applications. When attempting to rationalize physical or chemical properties associated with chiral molecules, the central problem is how chirality can be quantified for arbitrary molecular systems. Chiral molecules are usually characterized by measuring their optical rotation or circular dichroism spectra. Both methods are spectroscopic, involving interaction of the electromagnetic radiation with the electrons of the molecules. Although it would be desirable to deduce the absolute configuration from optical rotation measurements, this is not a simple matter.[2,3] One of the difficulties with optical rotation at a given wavelength depends on the fact that it represents a sum of oppositely-signed contributions from all the spectroscopic transitions in the chiral molecule. CD spectra allow in principle a study of the electronic transition of interest, but their use for assigning absolute configurations is often prevented by the fact that molecular orbital calculations for excited states are still far from being reliable. An alternative non-spectroscopic way of characterizing chiral molecules has recently been proposed based on the measurement of their twisting power in nematic liquid crystals.[4–9] It is known that addition of traces of a chiral solute to an achiral liquid crystal induces the formation of a helical superstructure characterized by its handedness and pitch. When the liquid crystal solvent is a nematic one, a 'twisted nematic' structure, traditionally termed rather improperly as 'cholesteric', is obtained. In the cholesteric phase, the local axis of preferential alignment (the 'director') rotates in space when moving along the helical axis. If the starting achiral mesophase is Smectic-C, where elongated molecules are organized in layers and the director is tilted away from the normal to the smectic planes, chiral solutes induce the chiral Smectic-C* phase. In such a phase, the projection of the director in the smectic planes rotates when moving perpendicularly to the planes. Equal amounts of enantiomeric solutes induce helical structures with identical pitch and opposite handedness. In the case of nematics, different substances show different abilities to twist the nematic phase, the twisting power of a given enantiomer being defined by eqn. (1), where p is the

$$1/\beta = \pm px \qquad (1)$$

pitch (in μm) and x is the mole fraction of dopant. Experimentalists generally define the dopant concentration in moles of solute per mole of solvent,[4] but on theoretical ground the use of the molar fraction is preferable; however, at the low concentrations for which the equation holds the two definitions are practically equivalent. In the above equation the signs + and − indicate right-handed and left-handed helices, respectively. The value of β is constant over a large interval of concentrations and changes with the nature of the solvent. The twisting power can therefore characterize 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.[6,7]

It is interesting to note that both optical rotatory power and twisting power, as physical manifestations of molecular chirality, have originated very recently new methods for assessing the chiral characters of particular probes, on the basis of their molecular shape. Ferrarini, Moro and Nordio[10–13] have developed a model able to relate the twisting power of a chiral solute to a 'helicity' tensor deduced from the probe shape, in addition to order and elastic properties of the nematic solvents. According to this model, the twisted shape of the chiral probe was assumed to exert a torque on the local nematic director, this effect being transmitted at distances of thousands of molecular lengths by virtue of the elastic properties of the nematic medium.[14] Osipov, Pickup and Dunmur[15] have taken the manifestation of optical activity as a basis for chirality indices. A second-rank gyration chirality tensor $\boldsymbol{G}$ was defined under the assumption that a point density at atomic positions could be substituted for the atomic polarizabilities. In terms of $\boldsymbol{G}$-tensor components two indices were obtained, the first being given by the tensor trace, and the second by the determinant of the corresponding traceless symmetric tensor. The two quantities were referred to as 'chirality index' and 'chirality anisotropy', respectively. Other authors have followed a somewhat different approach, on the basis that 'chirality' is a morphologic property susceptible of exact determination on mathematical grounds, independently of its physical manifestation. A critical review of the methods proposed to solve this problem has been recently presented by Mislow and co-workers.[16] A recently proposed method is based on the so-called continuous chirality measure, which essentially consists in representing a chiral object as a collection of connected vertices and by determining the minimal distance that vertices must move in order to attain the nearest achiral symmetry group.[17] The method represents a sophisticated variant of procedures where molecular chirality is simply measured by the overlapping volume when left and right enantiomers are maximally superimposed.[16]

Prediction of properties from molecular shape

The idea that 'chirality' is a morphological property susceptible of mathematical determination is not contradictory with the argument that approximate definitions of this property for an actual object of arbitrary shape can be given in an infinite number of ways. This conclusion can be easily understood by considering the problem of defining the shape of an achiral object. If we take a rectangular parallelepiped, there is obviously no problem: it suffices to give three side lengths, or the areas of three distinct faces. But if we consider, for instance, the solid model of the anthracene molecule, constructed as an assembly of van der Waals spheres, the choice is not so obvious. We might give the maximal lengths along the symmetry axes, or the areas of the surfaces obtained by projecting the molecule onto three orthogonal planes, but there is no simple relation between the two sets of data. For objects of lower symmetry, the task of defining the shape is even more complex. The problem is reminiscent of that encountered in crystal field theory: the functional form for the potential field generated by an assembly of electric charges can only be given as a series expansion, and the accuracy of the lowest order terms in representing the true potential field will depend upon the choice of the basis set. As a matter of fact, a cubic distribution is equivalent to a spherical one, at the lowest orders. In this spirit, we intend now to show that a particular second-rank pseudotensor, defined to interpret the twisting power of chiral probes when dissolved in liquid crystalline phases, provides a physically reasonable and a mathematically tractable description of the chiral character of a given molecule.

We shall therefore organize the paper as follows. At first, as an introductory example, we discuss an analytical solution to the problem of representing arbitrary molecular shapes, by developing the ideas outlined at the beginning of this section. This is achieved on the basis of the so-called surface tensor parametrization, which was introduced to interpret ordering properties of molecules in liquid crystal environments.[18,19] The surface tensor, a symmetric second-rank tensor, provides a useful description of the shape of a molecule, but it is unable to ascertain its chiral character; we shall therefore resort to the helicity tensor derived as an extension of the surface tensor concept. Apart from a discussion of a model chiral system, provided by a simple helix, numerical values of the surface and helicity tensors will be given for a number of chiral moieties, namely heptalene, biphenyl, binaphthyl, bianthryl and for the non-chiral tetramethylspirobipyrrolidinium ion. The numerical values of tensor components obtained by the mathematical model will be discussed in terms of experimental observables and molecular symmetry.

Shape models

The surface and helicity tensors

The surface and helicity tensors were derived in the context of the analysis of the orientational behaviour of molecules of arbitrary shape in liquid crystal environments.[10–13] The orienting potential experienced by the dissolved probe in a locally nematic phase was then taken as the integral over the molecular surface of contributions forcing the normal $\vec{s}$ to each surface element to align perpendicular to the local director $\vec{d}$. In the cholesteric phase the director rotates about an axis producing a helical macrostructure characterized by the pitch p. Thus, in a laboratory frame with the Y axis parallel to the helical axis, the director at the position $\vec{r}$ is defined by eqn. (2),

$$\vec{d} = \vec{u}_Z \cos(\vec{q}\cdot\vec{r}) + \vec{u}_X \sin(\vec{q}\cdot\vec{r}) \tag{2}$$

where $\vec{u}_Z$ and $\vec{u}_X$ are unit vectors along the X and Z laboratory reference axes and $\vec{q}$ is a vector parallel to the Y-axis of length $q = 2\pi/p$. A power expansion of the orienting potential for $q \longrightarrow 0$, justified by the large values of p compared to molecular dimensions, leads to the definition of a second-rank tensor $\boldsymbol{t}$, and a third-rank pseudotensor $\boldsymbol{q}^{(3)}$, with elements:[13]

$$t_{ij} = -\langle s_i s_j \rangle \tag{3}$$

and

$$q^{(3)}_{ijk} = -3\langle s_i r_j s_k \rangle \tag{4}$$

with s_i representing direction cosines of $\vec{s}$ in a molecular frame with the origin O at the origin of the laboratory frame and $\vec{r}$ the position vector of the surface element. The angular brackets denote integration over the molecular surface. In fact, the quantity of interest to correlate with molecular chirality is the symmetric part of the second-rank pseudo-tensor $\boldsymbol{q}$ associated with $\boldsymbol{q}^{(3)}$, whose elements are given by eqn. (5), where ε_{ikl} are

$$q_{ij} = -\sum_{k,l} \varepsilon_{ikl} \langle r_k s_l s_j \rangle \tag{5}$$

Levi–Civita symbols. In analogy with the results obtained for the roto-translation coupling tensor for an object of arbitrary shape,[20] a unique point R at which the tensor $\boldsymbol{q}$ is symmetric, always exists. The transformation law is given by eqn. (6), where

$$\boldsymbol{q}^R = \boldsymbol{q}^O - \vec{r}^{\,OR} \times \boldsymbol{t} \tag{6}$$

$\vec{r}^{\,OR}$ is the position vector of R relative to O. In the following the superscript will be neglected, with the implicit assumption that the origin of the molecular frame is in R. It should be recalled that pseudotensor components transform as direct products of polar vector and axial vector components, and Table 1 lists tensor components which are compatible with specific molecular symmetries,[21–23] for some selected point groups.

Table 1 Components of second-rank $\boldsymbol{A}$-tensors and $\boldsymbol{B}$-pseudotensors which transform according to the totally symmetric irreducible representation, for some selected enantiomorphous groups, and for all non-enantiomorphous groups which admit non-vanishing second-rank pseudotensor components

Enantiomorphous groups		
C_2	$A_{xx}, A_{yy}, A_{zz}, A_{xy}, A_{yx}$	$B_{xx}, B_{yy}, B_{zz}, B_{xy}, B_{yx}$
C_3, C_4	$A_{\parallel} = A_{zz}, A_{\perp} = (A_{xx} + A_{yy})/2$	$B_{\parallel} = B_{zz}, B_{\perp} = (B_{xx} + B_{yy})/2$
D_2	A_{xx}, A_{yy}, A_{zz}	B_{xx}, B_{yy}, B_{zz}
D_3, D_4	$A_{\parallel}, A_{\perp}$	$B_{\parallel}, B_{\perp}$
T, O, I	$\mathrm{Tr}\,\boldsymbol{A}$	$\mathrm{Tr}\,\boldsymbol{B}$
Nonenantiomorphous groups		
C_{h}	$A_{xx}, A_{yy}, A_{zz}, A_{xy}, A_{yx}$	$B_{xz}, B_{zx}, B_{yz}, B_{zy}$
$C_{2\mathrm{v}}$	A_{xx}, A_{yy}, A_{zz}	B_{xy}, B_{yx}
$D_{2\mathrm{d}}$	$A_{\parallel}, A_{\perp}$	$B_{xx} - B_{yy}$
S_4	$A_{\parallel}, A_{\perp}$	$B_{xx} - B_{yy}, B_{xy} + B_{yx}$

The tensors $\boldsymbol{t}$ and $\boldsymbol{q}$ have a straightforward geometrical interpretation. The element t_{ii} gives the contribution to the surface area of the molecule as viewed along the ith molecular axis, the sum of the diagonal elements t_{ii} being, apart from the sign, numerically equal to the surface area S, eqn. (7).

$$Tr\,\boldsymbol{t} = -S \tag{7}$$

The tensor component q_{ii} is the helicity along the i direction, *i.e.* the amount of surface rotation associated with translation along this direction. It has to be remarked that the two tensors are not exactly the surface tensor $\boldsymbol{T}$ and the helicity tensor $\boldsymbol{Q}$ defined in refs. 10–13, to which, however, they are related by the following expressions:

$$\boldsymbol{T} = \frac{3\boldsymbol{t} + S\mathbf{1}}{\sqrt{6}} \tag{8}$$

where $\mathbf{1}$ is the unit matrix, and

$$\boldsymbol{Q} = \sqrt{3/2}\,\boldsymbol{q} \tag{9}$$

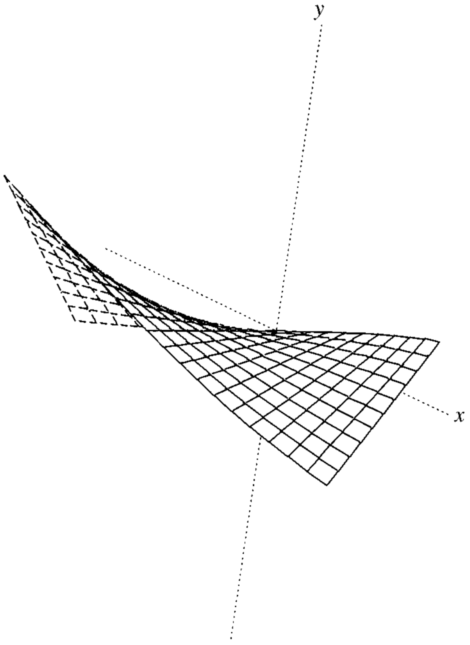

Fig. 1 Right-handed helix taken as a model in the text. The helix is obtained by twisting about the x axis a rectangle defined on the xz plane.

However, for the sake of simplicity, we shall refer in the following to the tensors $\boldsymbol{t}$ and $\boldsymbol{q}$, which will be also termed as surface and helicity tensor, respectively.

Numerical evaluation of $\boldsymbol{t}$ and $\boldsymbol{q}$ tensors is based on the definition of the molecular surface. This is accomplished by considering a molecule as an assembly of beads centred at the atomic positions, and assuming van der Waals radii for the beads.[24] However, it is worth emphasizing that the magnitude of both helicity and surface tensors is somewhat dependent upon the definition of the molecular surface. In fact, it has been suggested that some smoothing of the surface obtained by simple superimposition of van der Waals spheres may provide a better description of the exposed molecular surface.[25] For the sake of simplicity this effect is ignored here, but it will be discussed in a forthcoming paper.[26]

Model predictions for selected systems

To gain an insight into the physical meaning of surface and helicity tensors, it is useful to consider in some detail the example of the helix shown in Fig. 1, a simple chiral object obtained by counter-rotating about the x axis two opposite ends of a rectangle lying on the xz plane. The helix is characterized by $2\varphi_0$, the dihedral angle between the two ends. According to the usual convention, P and M labels are associated with the right- and left-handed helix, respectively, corresponding to opposite φ_0 values. The helix has D_2 symmetry and both $\boldsymbol{t}$ and $\boldsymbol{q}$ tensors are diagonal in a frame with the axes parallel to the C_2 axes. Fig. 2 shows the principal elements of the tensors for a right-handed helix of breadth 2 Å and length l_x equal to 6 Å, as a function of the angle φ_0. For $\varphi_0 = 0$ the helix reduces to a rectangle: thus both t_{xx} and t_{zz} vanish, and the t_{yy} component is equal to the whole surface area, changed in sign. Fig. 2(*a*) shows that with increasing twist angle the surface contribution perpendicular to the x axis remains close to zero, while the z component increases in absolute value and the y component correspondingly decreases. More interesting is the behaviour of the $\boldsymbol{q}$ tensor, displayed in Fig. 2(*b*). When considering a helix, the concept of helicity is naturally associated with the degree of distortion about the torsion axis. However, we see from the figure that the helicity about this axis comes out to be smaller than those about the z and y axes.

Table 2 Nonzero components of $\boldsymbol{t}$ and $\boldsymbol{q}$ tensors for P-biaryl structures with a 40° twist angle. The numerical values are in units Å^2 and Å^3 for $\boldsymbol{t}$ and $\boldsymbol{q}$ components, respectively. The z-axis coincides with a C_2 symmetry axis, and x is the principal axis of the $\boldsymbol{t}$ tensor closest to the inter-ring bond.

Biphenyl (D_2)				
	xx	*yy*	*zz*	*xy*
$\boldsymbol{t}$	−41.4	−89.6	−60.5	0
$\boldsymbol{q}$	2.1	31.3	−33.4	0
1,1′-Binaphthyl (C_2)				
	xx	*yy*	*zz*	*xy*
$\boldsymbol{t}$	−64.7	−129.7	−71.9	0
$\boldsymbol{q}$	5.6	50.0	−55.6	−8.6
$\boldsymbol{q}^a$	4.0	51.6	−55.6	0
1,1′-Bianthryl (C_2)				
	xx	*yy*	*zz*	*xy*
$\boldsymbol{t}$	−92.3	−173.2	−85.2	0
$\boldsymbol{q}$	4.5	81.2	−85.7	−17.2
$\boldsymbol{q}^b$	0.9	84.8	−85.7	0
9,9′-Bianthryl (D_2)				
	xx	*yy*	*zz*	*xy*
$\boldsymbol{t}$	−88.7	−169.3	−83.3	0
$\boldsymbol{q}$	18.2	65.7	−83.9	0

[a] Principal axis system of $\boldsymbol{q}$ obtained from that of $\boldsymbol{t}$ by rotation of *ca.* 10.5° about z. [b] Principal axis system of $\boldsymbol{q}$ obtained from that of $\boldsymbol{t}$ by rotation of *ca.* 12° about z.

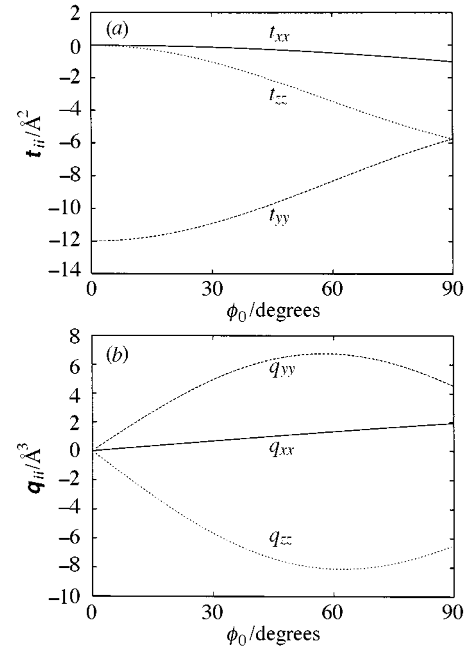

Fig. 2 Components of the tensors $\boldsymbol{t}$ (*a*) and $\boldsymbol{q}$ (*b*) for the helical surface of Fig. 1, as functions of φ_0, $2\varphi_0$ being the dihedral angle between the two ends of the helix. Breadth and length of the helix have been taken equal to 2 and 6 Å, respectively.

A similar helix-like behaviour is predicted for chiral molecules made up of two aromatic rings linked by a bond, which become chiral when the rings are not coplanar. Both surface and helicity tensors are functions of the twist angle between the aromatic moieties, and the helicity along the torsion axis, which is usually referred to when assigning the P, M labels, is also for these cases smaller than those along perpendicular axes.[12] Table 2 reports $\boldsymbol{t}$ and $\boldsymbol{q}$ components for P-configurations of biphenyl, 1,1′-binaphthyl, 1,1′-bianthryl and 9,9′-bianthryl with a twist angle of 40°. Obviously these are only hypothetical structures, because these molecules are characterized by torsional freedom about the ring–ring bond, and a given configuration can be stabilized only by suitable chemical substitution.[27] For the sake of comparison, the same value of 40° has been taken for all the biaryl systems examined here, even though it is physically justi-

Table 3 Nonzero components of **t** and **q** tensors for the chiral heptalene molecule and the nonchiral tetramethylspirobipyrrolidinium ion. The numerical values are in units Å^2 and Å^3 for **t** and **q** components, respectively. For both molecules the z-axis is taken along the C_2 symmetry axis. In the case of heptalene x is the principal axis of the **t** tensor in the direction of the long molecular axis, while for the tetramethylspirobipyrrolidinium ion, characterized by an axially symmetric **t** tensor, the x and y axes are taken parallel to the ring planes.

(M)-Heptalene (C_2)				
	xx	yy	zz	xy
t	−45.5	−61.5	−78.0	0
q	18.3	−34.8	16.5	4.9
q^a	18.7	−35.2	16.5	0
Tetramethylspirobipyrrolidinium ion (S_4)				
	xx	yy	zz	xy
t	−101.2	−101.2	−70.9	0
q	17.1	−17.1	0	12.6
q^b	21.2	−21.2	0	0

^{a} Principal axis system obtained from that of **t** by rotation of *ca.* 5° about z. ^{b} Principal axis system obtained by rotation of *ca.* 18° about z.

fied only for biphenyl-like molecules. The tensor components in Table 2 are expressed in the principal frame of **t**, unless specified otherwise. For the two structures with D_2 symmetry, *i.e.* biphenyl and 9,9′-bianthryl, **t** and **q** share their principal frames with the coordinate axes parallel to the three C_2 axes. In particular the axes are chosen in such a way that the x and z axes are parallel to the inter-ring bond and to the axis bisecting the acute dihedral angle between the aromatic moieties, respectively. For 1,1′-binaphthyl and 1,1′-bianthryl, which have C_2 symmetry, there is a single principal axis of **t** and **q** which is unambiguously defined by symmetry: it is parallel to the C_2 axis and is denoted as z. In both cases one of the principal axes of **t** comes out to be close to the ring-ring bond, and this is labelled as x. As far as the **t** tensor is concerned, we see from Table 2 that, as for the helix, the t_{yy} component is larger in absolute value than the others, which in turn tend to become equivalent for the most bulky derivatives. In analogy with the P-helix, the q_{xx} element is positive and smaller in absolute value than q_{yy} and q_{zz}, which increase in magnitude with the dimensions of the biaryl systems. By analogy with roto-translational coupling effects, one can easily understand that the helix in Fig. 1 is more effective as a propeller if it is allowed to spin around the y or z axis rather than the x axis. One can also notice that the y and z axes correspond to opposite spinning directions.

A somewhat more complex example of a chiral molecule is offered by the heptalene system, for which the existence of two opposite helicities perpendicular to the C_2 axis was previously recognized.[28] Even this molecule can be stabilized in a specific enantiomeric form by suitable substitution but, for the sake of clarity, we shall consider the simple heptalene skeleton, which exhibits a strongly distorted shape with alternation of single and double bond character in the peripheral carbon–carbon bonds. The numerical values obtained for **t** and **q** tensor components are reported in Table 3 for the M enantiomer, the configuration being now attributed according to the helicity along the bond common to the two rings.[28] Again, the tensors are expressed in the principal frame of **t** unless specified otherwise; the z axis is taken along the C_2 direction, and the y label is appointed to the axis closer to the bond common to the rings. By comparing the results obtained for heptalene with the data reported in Table 2, we see that the principal elements of the **t** tensor are close to those for biphenyl, and this is not surprising given the similar dimensions of the two molecules. However, the **q** tensors are rather different, the component q_{xx} being much larger in the case of heptalene. Fig. 3 shows the heptalene structure projected onto the principal planes of the helicity tensor, and this provides a picture of the helicities viewed along the three perpendicular axes, and an explanation for the relatively large value of q_{xx}, as discussed later.

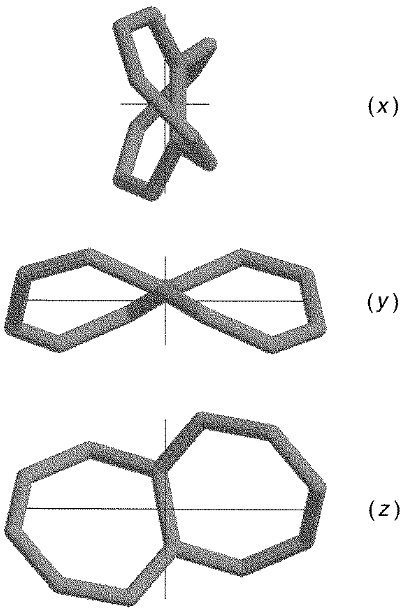

Fig. 3 Projections of the (M)-heptalene skeleton on the principal planes of the **q** tensor. The axes perpendicular to the various projection planes are indicated.

It is well known that a necessary condition for optical activity in the isotropic liquid phase is molecular enantiomorphism, *i.e.* the existence for the same molecule of two distinct configurations which are mirror images of each other. For rigidly oriented molecules, however, optical activity can occur in the nonenantiomorphous classes C_h, C_{2v}, D_{2d} and S_4.[22,29] Let us briefly treat as an example the case of a molecule belonging to the S_4 point group, the tetramethylspirobipyrrolidinium ion.[29] From Table 1 we find that linear combinations of second-rank pseudotensor components which transform according to the totally symmetric irreducible representation of S_4 are $B_{xx} - B_{yy}$ and $B_{xy} + B_{yx}$. Any pseudotensor will therefore be traceless and symmetric, and when expressed in a reference frame having as z-axis the rotation axis, it will have diagonal components $B_{xx} = -B_{yy}$ and $B_{zz} = 0$, because $B_{xx} + B_{yy}$, B_{zz} and $B_{xy} - B_{yx}$ do not transform according to the totally symmetric irreducible representation of the group. This obviously agrees with the fact that optical activity in isotropic solutions cannot be observed for molecules of S_4 symmetry. However, two principal axes x and y will exist, perpendicular to the rotation axis z but not directly identifiable by symmetry, corresponding to two nonzero principal values of the pseudotensor, equal in magnitude but opposite in sign. The results for the helicity tensor calculated for the tetramethylspirobipyrrolidinium ion and reported in Table 3 agree with this conclusion.

The examples presented here show how detailed information about molecular morphology, and molecular chirality in particular, can be obtained from the simultaneous analysis of the elements of the **t** and **q** tensors. It should be recalled that **q** is intrinsically traceless, thus two principal components must be given as independent information on the chiral character of a molecule. Chemists however are accustomed to use a single index (P-M, or R-S) to define the absolute configuration of a single enantiomeric form. It may be appealing to define a single pseudoscalar associated with the overall chirality content of the surface, *i.e.* a number which assumes the same absolute value but opposite sign for the two enantiomeric forms of a chiral molecule. The simplest way to obtain such an index, by using the same ingredients developed so far, is to take the following product:

$$\chi = -1000(q_{xx}t_{xx} + q_{yy}t_{yy} + q_{zz}t_{zz})/S^{5/2} \qquad (10)$$

Table 4 Chirality parameter χ and chirality order parameter $\mathcal{Q}$ calculated for various rigid structures. In the case of biaryls a 40° twist angle has been assumed. The $\mathcal{Q}$ values have been obtained according to eqn. (11), with orientational order parameters S_{ii} calculated from the molecular surface tensors and consistent with an orientational strength parameter $\varepsilon = 0.05$ Å^{-2}. This value corresponds for any nematic solvent to the same reduced temperature $T_{\text{red}} = T/T_{\text{NI}} \approx 0.95$, T_{NI} being the isotropic-nematic transition temperature.[12]

	χ	$\mathcal{Q}$/Å^3
(*R*)-CH_3CHFCl	0.006	0.006
(*R*)-CH_3CHFBr	0.008	0.010
(*R*)-CH_3CHFI	0.010	0.015
(*P*)-Biphenyl	1.7	5.0
(*P*)-1,1′-Binaphthyl	3.0	20.6
(*P*)-1,1′-Bianthryl	3.8	54.2
(*P*)-9,9′-Bianthryl	3.3	44.1
(*M*)-Heptalene	−0.05	−2.9
Tetramethylspirobipyrrolidinium	0	0

where the factor 1000 has been included to avoid numbers too small. From symmetry considerations it follows that the parameter χ vanishes for achiral systems. In addition, it has opposite signs for two enantiomers, as a consequence of the invariance of $\boldsymbol{t}$ and the change of sign of the $\boldsymbol{q}$ components. Similarity invariance[16] is ensured by the normalizing factor $S^{5/2}$, which makes the product independent of the molecular surface S. Table 4 reports χ values calculated for the systems discussed above, in addition to some chiral ethane derivatives.

For the sake of comparison, we have also reported in Table 3 the chirality order parameters $\mathcal{Q}$, defined as:[13]

$$\mathcal{Q} = -\sqrt{\tfrac{2}{3}}(Q_{xx}S_{xx} + Q_{yy}S_{yy} + Q_{zz}S_{zz}) \qquad (11)$$

where S_{ii} are the principal values of the molecule ordering matrix, which in turn is determined by the orienting potential defined in terms of the surface tensor.[10–13] The components Q_{ii} refer to the tensor defined in eqn. (9). The chirality order parameters have a direct physical meaning, since they are related to the helical twisting power of molecules dissolved in nematic solvents, eqn. (12), where K_{22}, v_{m} and ε are solvent

$$\beta = RT\varepsilon\mathcal{Q}/2\pi K_{22}v_{\text{m}} \qquad (12)$$

properties, namely, twist elastic constant, molar volume and orienting strength, respectively.

We see from Table 4 that high χ parameters are calculated for biaryls, with values which increase going from biphenyl to binaphthyl, and then to bianthryls. In the latter case, a lower chirality parameter is obtained for the most symmetric derivative. The extremely small χ values presented by ethane derivatives can be explained on the basis of the very low dissymmetry of the molecular surfaces. It is interesting to note that the χ values increase along the series Cl, Br and I, as expected on the basis of the increasing dimension of the substituent. The low values for both β and χ for heptalene results from cancellation of relatively large terms of opposite signs. Of course, χ vanishes for the tetramethylspirobipyrrolidinium ion, as it should.

Conclusions

The helicity tensor model illustrated in this paper provides a mathematically simple and physically acceptable descriptor of molecular chiral properties. Being based on the detailed description of the molecular surface, it appears more suitable than topological or combinatorial models for interpreting specific interactions of a dopant with its surroundings, or for studying quantitative structure–activity relationships. The analysis of the surface helicity is very accurate in comparison with models where the molecular shape is given only in terms of nuclear coordinates. Under this respect, it is worth noting that the Osipov model reflects the original physical basis, aimed at interpreting the optical activity by approximating the electronic distribution with delta functions peaked at the nuclear positions.[15]

When applied to the evaluation of twisting power for chiral probes in liquid crystals, the helicity tensor parametrization provides satisfactory quantitative predictions.[12,13] In fact, the model is so sensitive to the details of the molecular shape that it distinguishes between isomeric forms of substituted heptalenes differing only in the positions of the double bonds (see values reported for the heptalene derivatives 3 and 4 in ref. 12). For the cases of biphenyl and heptalene, which have not too dissimilar dimensions, it is interesting to note that the main difference between the calculated helicities reported in Tables 2 and 3 comes from the component relative to the long molecular axis, whose value is *ca.* 2 and 20 Å^3, respectively. This behaviour can be understood by considering that biphenyl resembles the helix discussed earlier, for which the helicity along the twisting direction is small, while the heptalene shape could be rather described as that of a flat ellipsoid twisted about the long axis. By looking at the heptalene molecules along the principal axes of the helicity tensor as drawn in Fig. 3, one can appreciate that the signs of the helicities reported in Table 2 agree with the usual convention leading to *P*, *M* labels.[28] Obviously, the advantage of the model is that of quantifying those helicities, so providing a criterion to distinguish between molecules of similar size but different shape. The model therefore provides a tool which can be useful in molecular engineering, for example by selecting suitable shapes to ensure the desired twisting power for optical devices, to optimize template–receptor interactions in stereospecific biochemical reactions and to guide the chemical synthesis of pharmaceutical products with specific functions. With this objective in mind, the pseudoscalar quantity χ defined in eqn. (10) is actually of little practical utility, apart from being expressed by a single rational number instead of a tensorial quantity. Not even the chirality order parameter $\mathcal{Q}$ is informative as a chirality index: it represents the helical twisting power of a chiral probe, a physical property which is the result of competing effects related to the shape of the probe and the orienting torques exerted by the anisotropic environment. As a matter of fact, variations of the ordering matrix components S_{ii} with temperature can even change the sign of the twisting power for a given molecular enantiomer.[12] Therefore, we should stress that complete information on the chirality properties of a molecule must be given in terms of the principal components of the helicity tensor.

One might inquire whether any relation can be found between the helicity tensor discussed here and that defining the rotational strength of optical transitions.[30] In fact, no relation can exist with the optical activity measured in isotropic solutions, because this has to do with the trace of the rotational strength tensor, and the $\boldsymbol{q}$-tensor we are dealing with here is traceless. Irreducible second-rank components[31] of the rotational strength tensor should in principle be compared with the components of $\boldsymbol{q}$, but it is unlikely to find any parallel between physically distinct properties, even if optical properties too might eventually be traced back to molecular shape.[32]

To conclude, a comment on the difference between helicity characteristics of molecules belonging to enantiomorphous and nonenantiomorphous groups may be useful. Symmetry requirements for the two categories are given in Table 1. All three principal values of $\boldsymbol{q}$ are generally nonzero in the enantiomorphous groups, while only two principal components of opposite sign are permissible for all nonenantiomorphous point groups. It may happen that even in enantiomorphic objects one of the principal values of $\boldsymbol{q}$ is accidentally zero, as in the case of the two-blade propeller discussed in ref. 12, and so in this particular case the two nonzero components will also have equal magnitude and opposite sign. Only molecules belonging to enantiomorphous groups can be termed chiral, because they can exist in two forms which are mirror images of each other. However, molecules belonging to nonenantiomorphous groups possess two perpendicular axes, along which 'helical' forms of opposite sign can be identified.[33] The two forms are related by a mirror plane which is also a symmetry plane, so that they correspond to distinct observables on the same object, which can actually be measured only if this is held rigidly in space. In principle, such systems could be studied in special liquid crystal phases, but early observations[34,35] in nematics have proven to be erroneous.[36]

Acknowledgements

The authors thankfully acknowledge Professors C. Corvaja and G. Gottarelli, and the E.C. fellow F. Janssen for stimulating discussions. The work has been supported by the HCM Contract N. 930282 and the PECO-NIS Contract N. 940602 of the European Community, and in part by the MURST and CNR through its Centro Studi sugli Stati Molecolari.

References

1 G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals*, Springer, Berlin, 1988.
2 S. F. Mason, *Molecular Optical Activity and the Chiral Discrimination*, Cambridge University, Cambridge, 1982.
3 J. H. Brewster, in *Topics in Stereochemistry*, eds. N. L. Allinger and E. L. Eliel, Wiley, New York, 1967, vol. 2.
4 G. Solladié and R. G. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 348.
5 G. Gottarelli, B. Samori, C. Stremmenos and G. Torre, *Tetrahedron*, 1981, **37**, 395.
6 G. Gottarelli and G. P. Spada, *Mol. Cryst. Liq. Cryst.*, 1985, **123**, 377.
7 G. Gottarelli, G. P. Spada and G. Solladié, *Nouv. J. Chim.*, 1986, **10**, 691.
8 H.-G. Kuball, T. Müller, H. Brüning and A. Schönhofer, *Mol. Cryst. Liq. Cryst.*, 1995, **261**, 205.
9 H.-G. Kuball, H. Brüning, T. Müller and A. Schönhofer, *J. Mater. Chem.*, 1995, **5**, 2167.
10 A. Ferrarini, G. J. Moro and P. L. Nordio, *Liq. Crystals*, 1995, **19**, 397.
11 A. Ferrarini, G. J. Moro and P. L. Nordio, *Phys. Rev. E*, 1996, **53**, 1.
12 A. Ferrarini, G. J. Moro and P. L. Nordio, *Mol. Phys.*, 1996, **87**, 485.
13 L. Feltre, A. Ferrarini, F. Pacchiele and P. L. Nordio, *Mol. Cryst. Liq. Cryst.*, 1996, **290**, 109.
14 P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford University, Oxford, 1974.
15 M. A. Osipov, B. T. Pickup and D. A. Dummur, *Mol. Phys.*, 1995, **84**, 1193.
16 A. B. Buda, T. Auf der Heyde and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 989.
17 H. Zabrodsky and D. Avnir, *J. Am. Chem. Soc.*, 1995, **117**, 462.
18 A. Ferrarini and P. L. Nordio, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1733.
19 A. Ferrarini, G. J. Moro, P. L. Nordio and G. R. Luckhurst, *Mol. Phys.*, 1992, **77**, 1.
20 J. Happel and H. Brenner, in *Low Reynolds Number Hydrodynamics*, Prentice Hall, Englewood Cliffs, New Jersey, 1965.
21 P. W. Atkins, M. S. Child and C. S. G. Phillips, *Tables for Group Theory*, Oxford University, Oxford, 1970.
22 D. R. Lovett, *Tensor Properties of Crystals*, Adam Hilger, Bristol and Philadelphia, 1989.
23 R. McWeeny, *Symmetry*, Pergamon, Oxford, 1963.
24 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
25 M. L. Connolly, *Science*, 1983, **221**, 709.
26 A. Ferrarini, F. Janssen, G. J. Moro and P. L. Nordio, *J. Phys. Chem.*, submitted.
27 G. Gottarelli, G. P. Spada, K. Seno, S. Hagishita and K. Kuriyama, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1607.
28 G. Gottarelli, H.-J. Hansen, G. P. Spada and R. H. Weber, *Helv. Chim. Acta*, 1987, **70**, 430.
29 J. K. O'Loane, *Chem. Rev.*, 1980, **80**, 41.
30 D. J. Caldwell and H. Eyring, *The Theory of Optical Activity*, Wiley Interscience, New York, 1971.
31 M. E. Rose, *Elementary Theory of Angular Momentum*, Wiley, New York, 1957.
32 J. F. Douglas and E. J. Garboczi, *Adv. Chem. Phys.*, 1995, **91**, 85.
33 M. J. Chern and R. A. Phillips, *J. Appl. Phys.*, 1972, **43**, 496.
34 R. Williams, *Phys. Rev. Lett.*, 1968, **21**, 342; *J. Chem. Phys.*, 1969, **50**, 1324.
35 H. Kimura, *J. Phys. Soc. Japan*, 1971, **30**, 1273; 1971, **31**, 623.
36 P. G. de Gennes, *Solid State Commun.*, 1970, **8**, 213.

Paper 7/02619F
Received 17*th April* 1997
Accepted 1*st October* 1997