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Twisting power of bridged binaphthol derivatives: comparison of theory and experiment

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The twisting ability of a novel series of bridged binaphthol derivatives with substituents of various lengths and chemical nature in the 6,6′-positions, recently synthesized and used as dopants in nematic solvents, is investigated with the help of the model based upon surface-helicity tensors. Structures of the low energy conformers of these compounds have been generated by molecular mechanics calculations. Their orientational behaviour and the coupling between anisotropy in the alignment and molecular chirality, which are at the origin of the helical twisting power, are analysed on the basis of the anisometry and the chirality of the shape.

1. Introduction

Chiral compounds dissolved in nematic solvents can induce cholesteric phases. The measure of their ability to produce twisted phases is the twisting power β, which is inversely proportional to the molar concentration of dopant c and to the cholesteric pitch p [1]:

$$\beta = \pm \frac{1}{cp}. \tag{1}$$

The magnitude of β for different solutes in a given solvent is a characteristic property of the chiral solute and its ordering in the liquid crystal matrix. An unusual example of chiral molecules is given by conformationally stable optical antipodes, called atropoisomers. In these compounds chirality originates from hindered rotation about single bonds. For example, in binaphthyl/binaphthol (BN) derivatives chirality results from the hindered torsional rotation about the 1,1′-C–C bond between the two naphthyl/naphthol moieties. BNs can be used as effective chiral dopants yielding highly twisted nematic mesophases [2–5]. BNs have also attracted attention as photo-racemisable dopants inducing a transition from cholesterics to compensated nematics [6]. The use of BN derivatives as molecular switches possessing a controllable degree of chirality seems to be very promising for electro-optic device application.

Just recently, a number of novel optically active BN derivatives with substituents of different lengths in the 6,6′-positions were synthesized. Two different classes of compound were obtained: open-chain BN-diethers and bridged BN-acetals [2, 3]. It has been shown that bridged compounds possess much higher twisting power than the open derivatives [2, 3]. In particular, the helical twisting power of BNs increases with increasing length of the substituents in the 6,6′-positions. The difference between the two classes of derivative, already observed in the past for similar compounds [5], has been attributed to the different aryl–aryl dihedral angles, whose value is about 45–55° for the constrained structures and not far from 90° for the open ones. The correlation between the twisting power of BN derivatives dissolved in nematic liquid crystals and the aryl–aryl dihedral angle was recently confirmed by theoretical predictions for unsubstituted model BNs [7, 8]: the maximum absolute value of β is predicted for dihedral angles of $\approx \pm 45°$ or $\approx \pm 135°$ between the naphthyl moieties, while $\beta \approx 0$ is found for the perpendicular arrangement (the planar geometry is of course achiral). In the present paper we shall limit our analysis to bridged derivatives, with the aim of rationalizing the effect of various substituents in the 6,6′-positions on the helical twisting power.

2. Theoretical model

The theoretical model has been presented elsewhere [7, 8]. Only a few expressions, relevant for understanding the results, will be summarized in the following.

An expression for the helical twisting power of chiral solutes in nematic solvents is obtained by a statistical mechanics derivation, based on the equilibrium between elastic distortion and solute–solvent interactions. The

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latter are described by a molecular field model, assuming that the normal **s** to each surface element of a molecule in a nematic environment tends to orient perpendicularly to the mesophase director **n**, according to a potential of general form $\varepsilon P_2(\mathbf{n}\ \mathbf{s})$, where P_2 is the second Legendre polynomial and ε is a parameter giving the orienting strength of the medium which, for a given mesophase, is a function of temperature. It can be shown [7, 8] that the orienting potential experienced by a molecule in a cholesteric phase with helical pitch p or corresponding wave vector $q=2\pi/p$, at the origin of the laboratory frame (X, Y, Z) having Y axis parallel to the helical axis and Z parallel to the director, is approximated in the limit $q\rightarrow 0$ by the following expression:

$$U(\Omega)/k_{\mathrm{B}}T = -\varepsilon\left(\frac{3}{2}\right)^{1/2}\sum_{ij} l_{Zi}(T_{ij}-qQ_{ij})l_{Zj}, \qquad (2)$$

where Ω are Euler angles for the rotation from the laboratory to a molecular (x, y, z) frame, and l_{Zi} is the cosine of the angle between Z and the i molecular axis. T_{ij} and Q_{ij} are cartesian components of traceless second-rank molecular tensors, defined as:

$$T_{ij}=\left[-3\int_S s_i s_j\,\mathrm{d}S + S\delta_{ij}\right]\Big/(6)^{1/2}, \qquad (3)$$

and

$$Q_{ij}=-(3/8)^{1/2}\sum_{k,l}\int_S [r_k s_l(\varepsilon_{ikl}s_j+\varepsilon_{jkl}s_i)]\,\mathrm{d}S, \qquad (4)$$

where δ_{ij} and ε_{ijk} are the Kronecker and the Levi–Civita symbol, respectively. The tensor **T** is called the surface tensor and measures the anisometry of the molecular surface; its diagonal elements are proportional to the surface areas perpendicular to the reference axes. According to equation (2), the **T** tensor is that mainly responsible for the orientational behaviour of the solute molecules, described by the ordering matrix $\boldsymbol{S}$:

$$S_{ij}=\int\frac{(3l_{Zi}l_{Zj}-\delta_{ij})}{2}P(\Omega)\,\mathrm{d}\Omega \qquad (5)$$

where $P(\Omega)$ is the orientational distribution function

$$P(\Omega)=\exp[-U(\Omega)/k_{\mathrm{B}}T]\Big/\int\exp[-U(\Omega)/k_{\mathrm{B}}T]\,\mathrm{d}\Omega. \qquad (6)$$

Ordering matrix and surface tensor have the same principal axis system, and the magnitude of the principal values of $\boldsymbol{S}$ is related to that of the corresponding **T** elements. The pseudotensor **Q** is denoted as the helicity tensor, since its diagonal elements represent helicities of the molecular surface viewed along the coordinate axes. The coupling between chiral features of the molecular surface and orientational ordering is described by the chirality order parameter $\mathscr{Q}$, defined as:

$$\mathscr{Q}=-(2/3)^{1/2}(Q_{xx}S_{xx}+Q_{yy}S_{yy}+Q_{zz}S_{zz}), \qquad (7)$$

where helicity tensor and ordering matrix are conveniently expressed in the principal frame of the latter. The chirality order parameter is the molecular quantity appearing in the expression for the helical twisting power β of a molecule in a given nematic solvent [7, 8]:

$$\beta = RT\,\varepsilon\mathscr{Q}/2\pi K_{22}v_{\mathrm{m}}. \qquad (8)$$

It is worth stressing that no free parameter enters equation (8) provided that a number of experimental data are available. These are the twist elastic constant K_{22}, the molar volume v_{m} and the ordering strength ε, which can be deduced from orientational order parameters [9].

3. Calculations

The binaphthol derivatives considered in the present work are listed in figure 1. The properties required to calculate their chirality order parameters and, consequently, their helical twisting powers, are the surface and the helicity tensors. According to equations (3) and (4), these depend only on the molecular surface. This was approximated as the outer surface of an assembly of van der Waals spheres centred at the nuclear positions [7]. A united atom description was used, with van der Waals radii taken from ref. [10]. Molecular mechanics calculations were performed to determine the molecular geometry of the compounds. In each case the initial geometry was generated by building fragments into a molecule using standard bond lengths and angles, and then minimizing the total energy of the molecule *in vacuo*. The BIOSYM package supplied with a Consistent Valence Forcefield (CVF91) was used in the calculations [11]. The parameters of this forcefield can be found in ref. [12]. This is a well-characterized and tested forcefield, widely used to simulate organic molecules. The following terms were considered in CVF91: (i) diagonal terms representing the energy of deformation of bond lengths, bond angles, torsion angles and out of plane interactions in a molecule, (ii) off-diagonal terms representing coupling between deformations of internal coordinates, (iii) non-bonded terms describing interactions between chemically unconnected atoms. The Discover-3 submodule of the BIOSYM package was used to perform the minimization of the total energy.

For all the derivatives under investigation the twist angle obtained between the naphthyl moieties was about 55°; this gives a first explanation of the large values of the measured helical twisting power [7, 8].

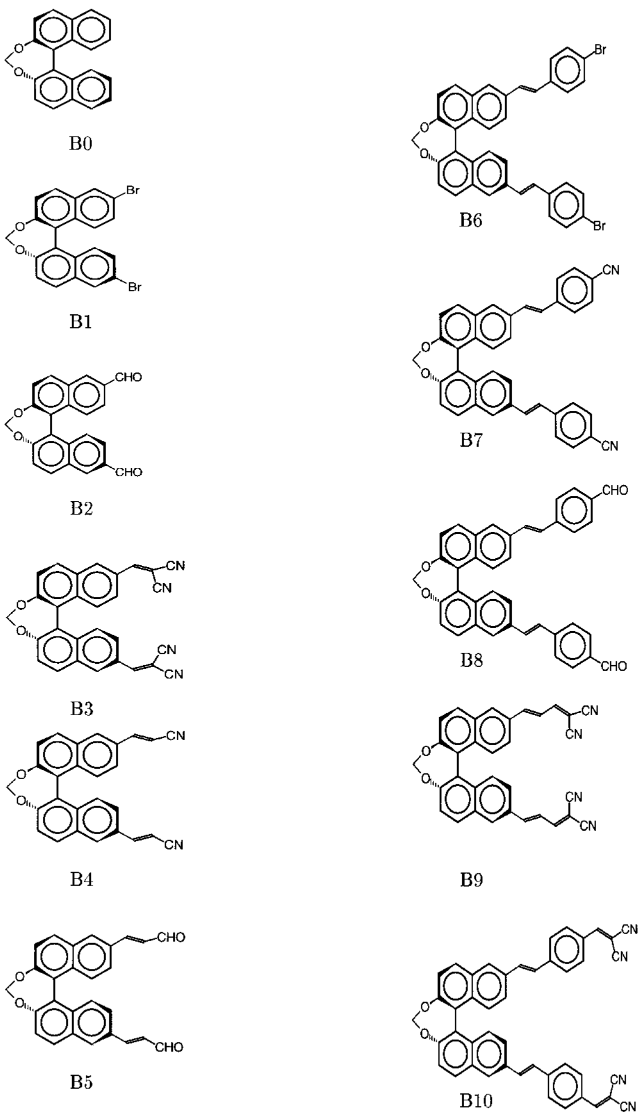


Figure 1. List of the binaphthol derivatives investigated in the present work.

For the derivative B2, the substituents in positions 6,6′ were found to lie in the plane of the corresponding naphthalene rings.

The conformation of the vinyl substituents in B4 and B5 is determined by the dihedral angles α_1, α_1' between each naphthalene ring and the plane of the attached vinyl group. For convenience of notation, we shall denote as *anti*- and *syn*- the conformations in which a vinyl group is directed towards the C_2 symmetry axis of the binaphthol core and on the opposite side, respectively. During the energy minimization a number of conformations corresponding to local energy minima were found, differing in the values of the dihedral angles α_1, α_1'. Four possible conformational states very close in energy were found for each angle, defined by values approximately equal to $\pm\overline{\alpha_1}$ (*anti*±) and $\pm(180-\overline{\alpha_1})$ (*syn*±), with $\overline{\alpha_1}=25°$–$30°$. For both B4 and B5 a *trans*-configuration at the vinyl bond was found.

The conformation of compounds with styryl substituents is determined by the angles α_1, α_1' and α_2, α_2', the latter being defined by the planes of the vinyl groups and the attached phenyl rings. Also for the angles α_2 and α_2' four minima very close in energy were found, at the same values reported for α_1 and α_1'. A *trans* configuration at the vinyl bond was predicted for all the compounds with styryl substituents.

Somewhat different arrangements were found for the derivatives with terminal $C(CN)_2$ groups. In the case of B9 the substituents were planar with both vinyl groups in the *trans*-configuration, and $\overline{\alpha_1}\approx 30°$. For B3 and B10 the angle between the planes of the $C(CN)_2$ groups and the attached aromatic rings was about 50°–55°; for B10 the values $\overline{\alpha_1}\approx\overline{\alpha_2}\approx 30°$ were obtained.

The results of our calculations are essentially in keeping with experimental data for 2-vinylnaphthalene and stilbene, which are the closest well-studied analogues of substituted BNs. From high field deuterium magnetic resonance experiments on 2-vinylnaphthalene in hydrocarbon solvents a value of 18° ± 3° for the angle between the naphthyl and vinyl planes was deduced, but no definite evidence for the relative stability of *syn*- and *anti*-conformers could be reached [13]. On the basis of ultraviolet spectroscopy data, 2-vinylnaphthalene appears to be a mixture of the two conformers, with a slight prevalence of the *anti*-form [14, 15]. In the case of stilbene, a dihedral angle of about 30° between the vinyl and the phenyl planes was estimated by electron diffraction studies in the gas phase [16], although in ref. [17] electronic absorption spectra of stilbene were interpreted by assuming a nearly planar geometry in liquid solution. In ref. [18] the conformation of donor–acceptor substituted stilbenes was found to depend on the nature of donor–acceptor combination, with the angle between the vinyl group plane and the benzene ring in the range 0–30°. In the light of the experimental and theoretical findings described above, the geometries calculated by CVF91 forcefield seem to be physically acceptable. However, since these structures were optimized *in vacuo*, changes due to the liquid crystal environment should be expected for both geometries and energies of the stable conformers.

In our analysis of binaphthol derivatives, the conformers generated with all possible combinations of the minima for the dihedral angles α_1, α_1', α_2, α_2' have been taken into account, and chirality order parameters have been calculated by averaging over all conformers, taken as equally probable. Actually, the complete distribution of conformational angles should be taken into account, or at least different weights should be used, especially for the case of the most sterically hindered derivatives, e.g. B3. However, by considering the small energy differences between the various conformers, and the fact that the energies in the nematic phases do not necessarily reflect those calculated *in vacuo*, the simplest approach has been followed, ignoring differences in the statistical weights. Therefore, comparison with experiment can be made only at a qualitative level, remembering also that the experimental data are affected by an error of about 15%.

4. Results and discussion

In presenting the results, we shall group the systems according to their size. Thus we shall start with the derivatives having no or relatively small substituents in the 6,6′-positions, that is B0, B1 and B2. Then the cases of B3, B4 and B5, which have substituents of intermediate lengths, will be discussed. As explained in § 3, a number of conformers is expected for these systems, corresponding to different values of the dihedral angles α_1. Due to the increased flexibility of the substituents, the situation becomes even more complicated in the case of the derivatives B6–B10, which will be dealt with at the end.

For these molecules, or for some selected conformers in the most complicated cases, we shall report the principal elements of the surface tensor **T**. The principal axes are labelled in such a way that z and y are the molecular axes with the largest tendency to align parallel to the local director, and perpendicular to it, respectively. The principal directions are different for the various structures; in all generality it is only possible to say that one axis is parallel to the C_2 symmetry axis when this exists, and that the y axis is approximately perpendicular to the plane bisecting the ring–ring dihedral angle (the approximate 'molecular plane'). We shall also report the principal elements Q_{aa}, Q_{bb} and Q_{cc} of the helicity tensor, and its diagonal elements in the principal frame of the surface tensor. In addition, we shall give the principal values of the ordering matrix $\boldsymbol{S}$ and the chirality order parameter $\mathcal{Q}$ calculated with $\varepsilon = 0{\cdot}05\,\text{Å}^{-2}$, a value corresponding to a situation of intermediate ordering [7]. For the sake of comparison, the twisting power β measured in the nematic solvent LC 1277, a mixture of alkyl- and alkoxy-cyanobiphenyls, at $T = 45$°C and $T = 55$°C [2, 3] is reported for the various derivatives.

4.1. *Derivatives with no or relatively small substituents: B0, B1, B2*

We shall start considering B0 and B1 whose properties, reported in the first columns of table 1, are very similar. From the analysis of the surface tensors, which have one large negative component, and two positive components close in magnitude, we can infer that these derivatives have a disc-like behaviour. For molecular shapes close to discs the relation $T_{yy} \approx -2T_{xx} \approx -2T_{zz}$ holds, and the alignment corresponds to the y axis perpendicular to the director. We can see however from the table that for

Table 1. Ordering and chirality properties calculated for BN derivatives: principal elements of the surface tensor **T**, diagonal elements of the helicity tensor **Q** in the principal axis system (x, y, z) of the surface tensor and in its principal frame (a, b, c), and principal values of the ordering matrix $\boldsymbol{S}$ calculated with $\varepsilon = 0{\cdot}05\,\text{Å}^{-2}$. For B2 all possible conformers are considered, while for B5 and B6 only a few are selected (see text). The molecular z axis is that corresponding to the largest positive principal value of the ordering matrix $\boldsymbol{S}$.

	Molecule									
Parameter	B0[a]	B1[a]	B2(A)[a]	B2(B)[a]	B2(C)[b]	B5(A)[b]	B5(B)[a]	B5(C)[a]	B6(A)[b]	B6(B)[b]
$T_{xx}/\text{Å}^2$	17	22	19	21	22	16	19	17	30	22
$T_{yy}/\text{Å}^2$	−42	−45	−47	−46	−45	−59	−49	−59	−81	−88
$T_{zz}/\text{Å}^2$	25	24	28	25	23	43	31	42	51	63
$Q_{xx}/\text{Å}^3$	−93	−96	−96	−97	6	13	−71	−109	−40	125
$Q_{yy}/\text{Å}^3$	83	90	93	98	105	119	136	88	252	−15
$Q_{zz}/\text{Å}^3$	10	6	3	−1	−111	−132	−65	21	−213	−110
$Q_{aa}/\text{Å}^3$	−93	−96	−96	−104	−3	−19	−115	−109	−67	−88
$Q_{bb}/\text{Å}^3$	83	106	101	108	114	151	176	122	280	198
$Q_{cc}/\text{Å}^3$	10	−10	−5	−4	−111	−132	−61	−14	−213	−110
S_{xx}	0·09	0·15	0·09	0·12	0·16	−0·06	0·06	−0·05	−0·01	−0·15
S_{yy}	−0·31	−0·32	−0·33	−0·33	−0·33	−0·37	−0·34	−0·37	−0·40	−0·41
S_{zz}	0·22	0·18	0·24	0·21	0·17	0·42	0·28	0·42	0·41	0·56
$\mathcal{Q}/\text{Å}^3$	26	34	32	38	42	83	56	15	153	61

[a] z axis close to the ring–ring bond (see figure 2).
[b] z axis along the C_2 symmetry axis (see figure 3).

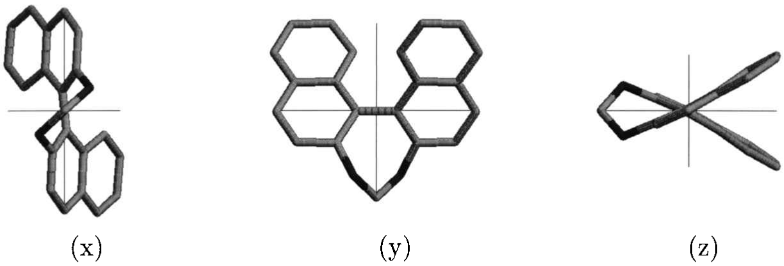


Figure 2. Projections of the binaphthol derivative B0 on the principal planes of the surface tensor **T**. Under each projection the axis perpendicular to the projection plane is indicated.

B0 and B1, the two principal directions perpendicular to the y axis are not fully equivalent. In both cases the z axis, which according to our convention is that with the stronger tendency to lie parallel to the local director, is close to the naphthol–naphthol bond. Considering now the helicity tensor we see that for both B0 and B1 high helicity values, approximately equal in magnitude and opposite in sign, are obtained for the axis perpendicular to the approximate 'molecular plane' and for the axis parallel to the C_2 symmetry axis, while only a low helicity results along the ring–ring bond. This is a general behaviour for chiral systems obtained by rotating two planar moieties about a common axis [7]. We can also infer from table 1 that for both B0 and B1 the principal frames of the **T** and **Q** tensors are very close, with the C_2 axis common to the two reference systems. Figure 2 shows the projections of B0 on the principal planes of the surface tensor. Analogous projections are not shown for B1, since they would look very much the same as for B0. In view of the disc-like structures, the helicity of the cholesteric phases induced by these solutes are expected to be determined by the sign of the molecular helicity about the y axis. In fact, for disc-like systems $S_{xx} \approx S_{zz}$, so that, the tensors **Q** and ***S*** being traceless, equation (8) can be rewritten as $\mathscr{Q} \approx -(3/2)^{1/2} S_{yy} Q_{yy}$. Since Q_{yy} is positive and S_{yy} is negative, positive chirality order parameters are expected for B0 and B1, in agreement with the sign of the measured twisting power [2, 3].

For the derivative B2 the situation is slightly more complicated, because of the possible rotations about the naphthyl–carbonyl bonds. In the structures derived from energy minimization calculations each aldehydic group lies in the same plane as the attached aromatic ring. Although the planar arrangement of an aldehydic substituent linked to an aromatic ring is reasonable, as confirmed by geometry optimizations for simpler systems, there seem to be no reasons in favour of a particular orientation of the CO group within the plane. Therefore we have considered the planar structures obtained by taking all possible directions of the CO groups. Using the same notation introduced in § 3 for vinyl substituents, we shall denote as *anti* and *syn* the carbonyl conformations having the CO group directed towards and against the C_2 symmetry axis, respectively. There are three possible conformers: one with both CO groups *syn*, B2(A), two with a CO *syn* and the other *anti,* B2(B), and one with both CO *anti* B2(C). Again we can see from table 1 that all the conformers have a disc-like behaviour; however, we can also see that small structural changes can affect the preferred orientation and, as a consequence, the twisting power. The properties of B2(A) will not be discussed, because they are very close to those of B1, apart from a more pronounced difference between the T_{xx} and T_{zz} components, resulting in a stronger preference for z alignment. The effect of a π rotation of both carbonyl groups is that of reducing the biaxiality in the molecular plane and shifting the axis of preferential aligment from the ring–ring bond in B2(A) to the direction of the C_2 axis in B2(C) (see figure 3). We have adopted the convention of labelling as z the axis corresponding to the largest principal value of the ordering matrix ***S***; therefore the x and z labels for B2(C) are interchanged with respect to those adopted for B2(A). It follows that the helicity values 6 and -111 for B2(C) must be compared with 3 and -96 for B2(A), which are rather close, as expected. However, the slight increase of the principal helicities has the effect of

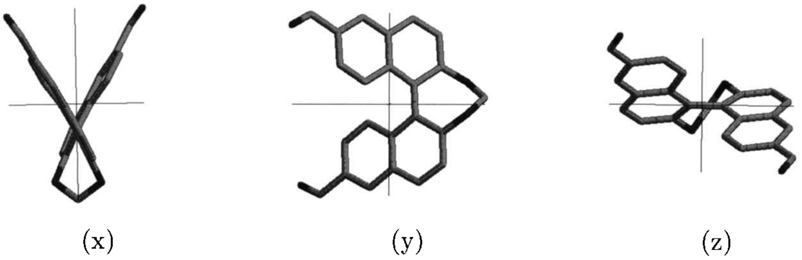


Figure 3. Projections of the conformer (C) of the binaphthol derivative B2 on the principal planes of the surface tensor **T**. Under each projection the axis perpendicular to the projection plane is indicated.

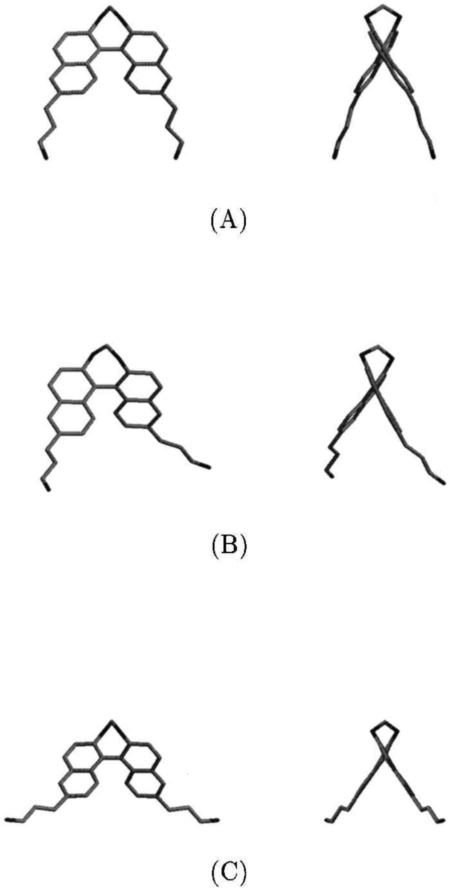
producing a significant increase in twisting power passing from the *syn*- to the *anti*-conformer. In the case of the (B) conformers the reduced symmetry of the structure leads to small changes with respect to both B2(A) and B2(C), which result in a chirality order parameter intermediate between the values obtained for the two other conformers.

The first three columns of table 2 show the chirality order parameters obtained for B0, B1 and B2; in the latter case the average over four conformers, taken with equal weight, has been performed. We can see that, in agreement with the experimental twisting power data also reported in the table, the $\mathcal{Q}$ values are positive and very similar for the derivatives B1 and B2, and larger than the value predicted for the unsubstituted compound.

4.2. *Derivatives with substituents of intermediate length: B3, B4, B5*

For the derivatives B3–B5 we have considered the 16 conformers which were generated by taking all combinations of the four possible values $\pm\overline{\alpha_1}$, $\pm(180^\circ - \overline{\alpha_1})$, for each of the dihedral angles α_1 and α_1' between the naphthyl and the vinyl planes. A pronounced dependence of the chirality order parameter upon the substituent conformation was found with values ranging between 20 and 80 Å^3 for B4 and B5, and between 25 and 55° Å^3 for B3. The different behaviour of B3 is due mainly to the larger deviation from planarity of the naphthyl–vinyl dihedral angles predicted for this derivative. In all cases the highest chirality order parameters are predicted for a planar arrangement of the vinyl groups, and a lowering is expected for increasing $\overline{\alpha_1}$ values. The presence of the two CN substituents linked to the vinyl groups has the effect of reducing the differences among the various conformers in the case of B3.

According to their chirality order parameter, the conformers can be roughly divided into three classes: conformers with low, high and intermediate twisting power. If we look at their structures we see that, in close analogy with what as already been seen for the derivative B2, the three classes correspond to [*syn*, *syn*], [*anti*, *anti*] and [*syn*, *anti*] or [*anti*, *syn*] conformers, respectively. In order to get some more understanding we shall consider in detail the conformers (A) [*anti*−, *anti*−], (B) [*anti*+, *syn*+] and (C) [*syn*+, *syn*+] of B5, whose structures are shown in figure 4. The same three conformers are considered in the columns four to six in table 1. From a comparison with the first three columns, it appears that for these conformers the **T** tensor elements, and hence the order parameters, are slightly larger and more biaxial than for the smaller derivatives B0, B1 and B2. An analogous increase is shown by the


(A)

(B)

(C)

Figure 4. Structures of the conformers (A), (B) and (C) of the derivative B5.

Table 2. Chirality order parameter calculated with $\varepsilon = 0{\cdot}05$ Å^{-2} for the BN derivatives. In all cases but B0 and B1, the average value over all the conformers, obtained as explained in the text, is given. Experimental twisting power values [2, 3] are also reported.

	Molecule										
Parameter	B0	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
$\mathcal{Q}$/Å^3	26	34	38	33	51	52	94	94	93	79	84
β/µm^{-1} (exp/$T = 45°$)	46	56	59	77	67	79	105	85	91	103	115
β/µm^{-1} (exp/$T = 55°$)	48	56	54	80	70	79	105	87·5	91	105	112

Q tensor elements. Furthermore, these results confirm the analogy already mentioned with the conformers of B2. Of course, here the effects are emphasized by the presence of the longer substituents. In order to make a comparison with experimental data, we have reported in table 2 the chirality order parameter obtained for B3, B4 and B5 by averaging over all the conformers. We can see that, in agreement with experiment, they are larger than those for the derivatives B0–B2. A somewhat low value is predicted for B3, and this is essentially due to the value of the dihedral angles between the naphthyl and vinyl groups, which might be underestimated by the minimization procedure. For the sake of comparison, we have also performed calculations for conformers of B3 generated taking $\overline{\alpha_1} = 30°$, and a $\mathcal{Q}$ value of 58 Å^3, in better agreement with the other data, has been obtained.

4.3. *Derivatives with long substituents: B6–B10*

Again, for each derivative all the conformers, obtained as explained in § 3, have been considered: they amount to 256 for B8, and they reduce to 64 for B6 and B7, due to the presence of a symmetry plane perpendicular to the phenyl rings in the side groups, which makes $syn\pm = anti\mp$ for the angles α_2 and α_2'. Actually, not all of these conformers are different, but all of them have to be retained to contribute to the average with the correct weight. It results from our calculations that the chirality order parameters of the various conformers range between -5 and 155 Å^3. Larger variations than in the case of the derivatives B3–B5 are not surprising, because a change in the orientation of the bulky phenyl substituents can be expected to affect the ordering and chiral properties in a significant way. We shall focus on the eight conformers with a C_2 axis, for which symmetry makes the results more easily understood. Within this set of conformers the highest chirality order parameters correspond to structures with: (i) an [*anti*, *anti*] conformation at the α_1 angles, i.e. the conformers most elongated along the C_2 axis, as already seen for derivatives with shorter substituents; (ii) the aromatic rings attached to a vinyl group lying on the same side of the vinyl plane. As an example we have reported in the two last columns of table 1 properties of the conformers [*anti*−, *anti*−] [*syn*−, *syn*−] (A) and [*anti*−, *anti*−] [*syn*+, *syn*+] (B) of B6, where the two labels refer in the order to the [α_1, α_1'] and [α_2, α_2'] dihedral angles. These are two elongated conformers, differing in the conformation of the terminal rings: in (A) the aromatic rings attached to a vinyl group lie on the same side of the vinyl plane, while they lie on opposite sides in (B). In the case of the conformer (A), the tensors **T** and **Q**, which have large principal components, approximately share the same principal frame, with axes close to those shown in figure 3 for B2(A). This is in keeping with the trend already observed for the symmetric conformers of derivatives with shorter substituents. In fact we have seen that, at least for symmetric conformers, the principal components of the surface and helicity tensor increase with increasing dimension of the substituents, and the principal frames of **T** and **Q** are very close, with the axes directed as in figures 2 or 3 according to whether the conformer is elongated in the direction of the C_2 axis, or perpendicular to it. On the other hand, the helicity tensor can change significantly when the terminal phenyl groups of long substituents give a contribution opposing that of the central core. This is shown by the conformer (B): while the surface tensor is similar to that of the conformer (A), the helicity tensor is markedly different. In particular, for the (B) conformer, the principal axis systems of **Q** and **T** are no longer close to each other, differing by a rotation of *c*. 45° about the C_2 symmetry axis, as shown in figure 5. Furthermore, the principal values of **Q** are comparable with those of derivatives with shorter substituents.

The considerations on the conformers (A) and (B) could be generalized to all the symmetric conformers with high and low $\mathcal{Q}$, respectively. As already seen in other cases, the conformers which lack any symmetry element have intermediate $\mathcal{Q}$ values.

For the derivative B9, 16 conformers have been considered, as for the systems B3–B5. Their chirality order parameters have the same trend as for B3, but they are larger in magnitude. This is only partly a consequence of the increased dimension, which leads to an increase of the **T** and **Q** tensor components, the occurrence of

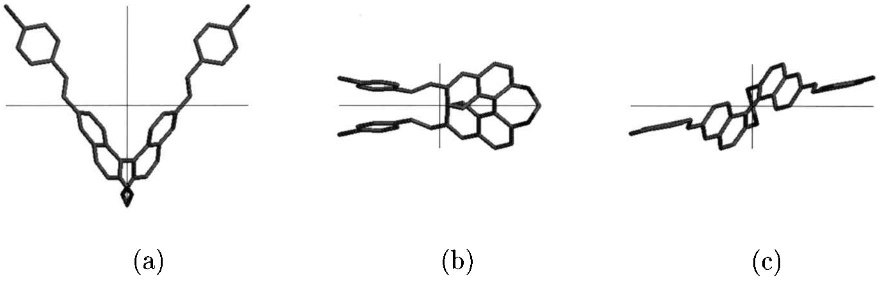


Figure 5. Projections of the (B) conformer of B6 on the principal planes of the helicity tensor **Q**. Under each projection the axis perpendicular to the projection plane is indicated.

larger deviations from planarity for the α_1, α_1' dihedral angles being the main reason.

Finally, for the derivative B10 the number of possible conformers rises to 1024, because of the additional freedom for the angle between the phenyl group and the terminal double bond. Of course they cannot be analysed in detail; it will suffice to say that the considerations presented for B6 can also be generalized to this derivative.

The average chirality order parameters calculated for the derivatives B6–B10 are reported in the last five columns of table 2, together with the measured helical twisting powers [2, 3]. We can see that they are very high, definitely higher than those for all other compounds of the series. As for the case of B3, for B10 also calculations have been performed with $\overline{\alpha_3} = 30°$, and $\mathcal{Q} = 105\,\text{Å}^3$ has been obtained.

5. Conclusion

We have seen that, on the basis of the geometrical structures, it is possible to get a clear understanding of the twisting ability of bridged binaphthol derivatives. First of all, the value of the naphthol–naphthol twist angle, about 55°, immediately provides an explanation for the high measured twisting powers. In fact, the theoretical curve of the helical twisting power as a function of the twist angle for binaphthyl has vanishing values corresponding with the perpendicular and planar geometries, and shows maxima at about ±45° [8].

Going into more detail, the trend along the series can also be understood. In the absence of detailed information on elastic constants, ordering strength and molar volume of the solvent, which would be required for an accurate evaluation of the factor relating chirality order parameter $\mathcal{Q}$ and helical twisting power β, we must be content with the fact that the scaling factor, obtained by a linear least-squares procedure, comes out to be 1·2, which is of the correct order of magnitude. In fact, a value in the range between 1 and 2 is expected for $K_{22} = 2\text{–}3 \times 10^{-12}$ N, $v_{\mathrm{m}} = 3 \times 10^{-4}\,\mathrm{m}^3\,\mathrm{mol}^{-1}$ and $\varepsilon = 0{\cdot}04\text{–}0{\cdot}06\,\text{Å}^{-2}$, which are reasonable for a mixture of alkylcyanobiphenyls, such as the solvent LC 1277. Experimental data and scaled chirality order parameter values are shown in figure 6 for all the binaphthol derivatives under examination. We have also indicated by diamonds the results obtained for the derivatives B3 and B10 giving $\overline{\alpha_1}$ and $\overline{\alpha_3}$, respectively, the value 30°, smaller than that obtained from energy minimization. It appears that the experimental trend along the series is reproduced, with twisting powers which increase with increasing length of the substituents. It should be emphasized that this result is by no means obvious, and completely wrong conclusions could be drawn on the basis of calculations performed on a single conformer. The agreement apparent from figure 6 shows indeed that the molecular systems examined here exhibit a rich conformational isomerism, and very accurate potential surfaces, appropriate for the anisotropic enviroment, are required for a more quantitative analysis of the experimental twisting power data.

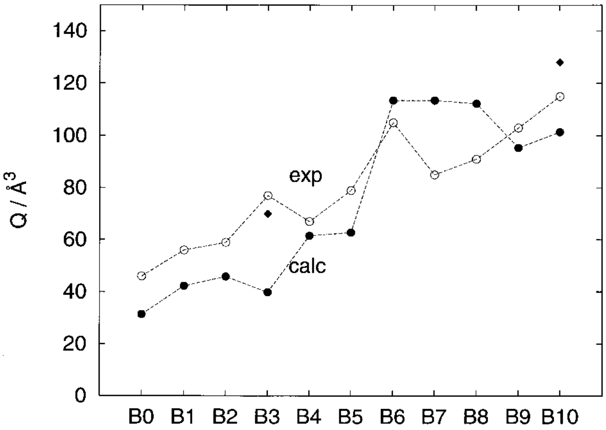


Figure 6. Scaled $\mathcal{Q}$ values (filled circles) and twisting power values measured at $T = 45°$ (open circles). In each case, the line connecting points is drawn as a guide for the eye. Diamonds represent the scaled $\mathcal{Q}$ values obtained for B3 and B10 for special choices of the dihedral angles between the aromatic ring and the plane of the attached $\mathrm{C=C(CN_2)}$ group (see text).

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