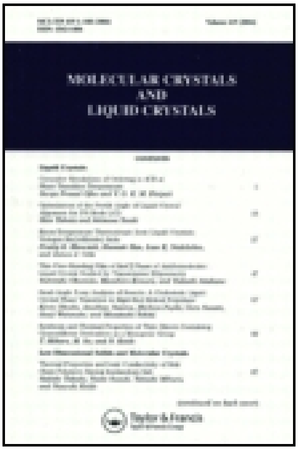

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Some Calculations of Molecular Chirality

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Some Calculations of Molecular Chirality

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Chirality of optically active liquid crystal molecules has become an important research topic. Different approaches, both theoretical and experimental have been undertaken to create a better understanding of the concept of chirality in liquid crystals. Surprisingly good agreement is found from predictions from single molecules for phase properties. The scaled chiral index with no solvent interaction has been successful in predicting the helical twisting power of a range of dopants in nematic solvents. We present here results for both single molecule studies and molecular dynamics simulations for two biphenyl dopants and discuss the effect of conformational change on the predictions of the scaled chiral index of helical twisting power.

Keywords: chiral dopant; helical twisting power; scaled chiral index

1. INTRODUCTION

Different approaches have been undertaken to create a better understanding of the concept of chirality. These vary from experimental such as [1] to theoretical such as [2–10] to studies of single molecules such as [8,11] to simulation studies of mixtures such as [12]. The single molecule studies either of the optimized geometry of a molecule such as [8,14] or of conformational averages of a property [11,12] allow calculation of the helical twisting power (HTP)

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values for a range of chiral dopant molecules consistent with experimentally determined values. The results for a single optimised geometry for a range of helicene and binapthyl molecules have been surprisingly successful [13–15] providing evidence that the dopant molecule geometry may be considered to be the major influence upon helical twisting power in some solute-solvent interactions. We present here calculations of a scaled chiral index G_{0S}, [7,8], described in section two, both for a single optimized geometry and for conformational averages from gas phase molecular dynamics simulations for two biphenyl molecules. These have more substituent groups that are able to rotate relative to the ring carbons than the binapthyl and helicene molecules previously considered. They present a more difficult challenge since their twisting power varies from small to high magnitudes as well as in sign. We consider two biphenyls selected from a group of eight because they have a small magnitude helical twisting power and opposite sign for G_{0S} to the experimental value. We examine in particular the effect of flexibility by considering conformational averages. We compare results for both calculations in section three and also make comparison with experimental values of relevant HTP values. Conclusions are presented in the final section.

2. AVERAGE SCALED CHIRALITY MEASURE

The link between chirality at the molecular level and the structure of chiral phases is not well understood. A recent approach, which calculates chirality parameters for a molecular structure is employed by Lubensky *et al*. [9] and by Osipov, Pickup and Dunmur [7]. The mathematical formulation developed by Osipov *et al*. [7] defines the gyration tensor

G for a molecule as

$$\mathbf{G} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rho(\mathbf{r}_3)\rho(\mathbf{r}_4) \times \frac{[(\mathbf{r}_{12} \times \mathbf{r}_{34}) \otimes \mathbf{r}_{14}](\mathbf{r}_{12} \cdot \mathbf{r}_{23})(\mathbf{r}_{23} \cdot \mathbf{r}_{34})}{(r_{12}r_{23}r_{34})^n r_{14}^m} \tag{1}$$

where each $\mathbf{r}_i$ ranges over the volume occupied by the molecule, ρ is some quantity associated with the molecule, for example mass density, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and $\mathbf{r}_{ij} = \mathbf{r}_{ij}/\mathbf{r}_{ij}$ and n and m are arbitrary integers. From this tensor is extracted the isotropic chirality index

$$G_0 = \frac{1}{3}\mathrm{Tr}\mathbf{G} \tag{2}$$

$$= \frac{1}{3}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rho(\mathbf{r}_3)\rho(\mathbf{r}_4)$$

$$\times \frac{[(\mathbf{r}_{12} \times \mathbf{r}_{34}) \cdot \mathbf{r}_{14}](\mathbf{r}_{12} \cdot \mathbf{r}_{23})(\mathbf{r}_{23} \cdot \mathbf{r}_{34})}{(r_{12}r_{23}r_{34})^n r_{14}^m} \tag{3}$$

This quantity is invariant under rotation and translation, changes sign on reflection, is non-zero only for chiral objects and has properties under dilation that depend on the values of $m$and n. However, it scales as N^4 for an N point mass representation of a molecule. Some of the authors extended this formulation (Eq. 3) in [8] for general molecular structures by calculating a scaled chiral index $G_{0S} = 1/3\ 4!/N^4 G_0$, that tends to a fixed value with increasing N. When we consider real molecules we require the discrete form of the isotropic scaled chirality index G_{0S} which sums the contribution of all sets of four atoms in a numerical evaluation given by:

$$G_{0S} = \frac{4!}{N!}\frac{1}{3}\left[\sum_{\substack{\textit{all permutations of}\\ i,j,k,l=1\ldots N}}^{N} w_i w_j w_k w_l \frac{[(\boldsymbol{r}_{ij} \times \boldsymbol{r}_{kl}) \cdot \boldsymbol{r}_{il}](\boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{jk})(\boldsymbol{r}_{jk} \cdot \boldsymbol{r}_{kl})}{(r_{ij}r_{jk}r_{kl})^n r_{il}^m}\right] \tag{4}$$

The atomic weights w_i, w_j, w_k, w_l are values of physical quantities associated with different atoms, set to 1.0 here. If $n = 2$ and $m = 1$ the index is dimensionless (invariant under dilation) and it is this form we shall consider.

For relatively rigid molecules the scaled chiral index $-G_{0S} \times 10^4$ has been successful in predicting helical twisting power from one optimized geometry [8,13]. In the case of flexible molecules each conformation m from the total population M is characterised by a scaled index G_{0Sm}. We then calculate the average scaled chiral index $<G_{0S}>$ from a molecular dynamics simulation as:

$$<G_{0S}> = \frac{1}{M}\sum_{m=1}^{M} G_{0Sm} \tag{5}$$

and scale by $\times -10^4$ to make comparison simple with experimental values of helical twisting power typically in the range $\pm$ 0–100 μm^{-1}.

3. FLEXIBLE LIQUID CRYSTAL CHIRAL DOPANTS

Liquid crystal dopants are used to aid the synthesis of materials with high macroscopic helical twisting power (β_M) [16] given by:

$$\beta_M = (p\ c_w\ r)^{-1} \tag{6}$$

where p is the helical pitch, c_w is the concentration (moles of dopant per mole of solvent) and r the enantiomeric purity of the dopant. We consider here two flexible biphenyl dopants as illustrated in Figure 1 below.

Both molecules have substituent methyl or methoxy tails with more freedom to rotate than the parent biphenyl molecules but the molecule with sulphur substituents has fewer subtituents. Their relative experimental helical twisting powers are +8 and −6 respectively. The optimised geometry for each biphenyl molecule was obtained by minimising the energy using a semi-empirical quantum mechanical package CACHe [18] with the MM3 force field. The scaled chiral index, $-G_{0S} \times 10^4$ was then calculated for each dopant and is given in Table 1. It is apparent that whilst the magnitude is approximately correct for these small values the signs are reversed. This is the first published example of $-G_{0S} \times 10^4$ predicting an incorrect sign. In the case of six other biphenyl molecules with a range of substituents the correct sign was predicted [21].

The optimized geometry of the two molecules considered here is similar in energy to many other of their conformations and it may be that a more accurate estimator of the helical twisting power is an

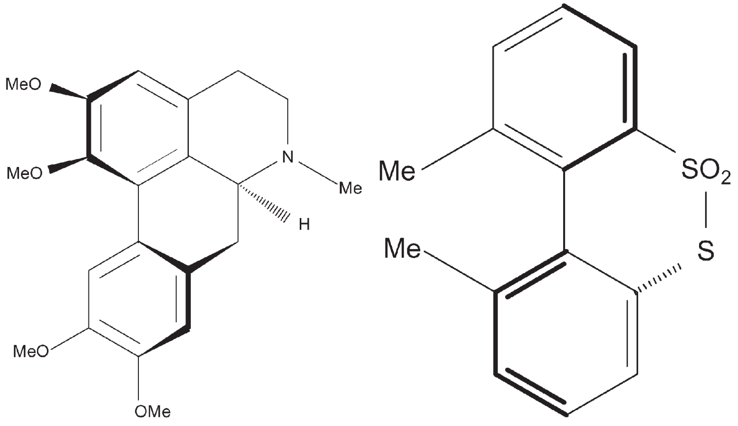

FIGURE 1 Chemical structure of the biphenyl molecules.

TABLE 1 Values of Helical Twisting Power from Experiment [17] and Computer Simulation of two Biphenyl Dopants and Calculated Scaled Chiral Indices for an Optimised Geometry $-G_{0S} \times 10^4$ and an Average $-\langle G_{0S}\rangle \times 10^4$ from the MD Simulation

Molecule	$\beta_m(\text{Exp})/\mu\text{m}^{-1}$	$-G_{0S} \times 10^4$	$-\langle G_{0S}\rangle \times 10^4$
A	+8	−6.0	−11.3 (15)
B	−5	+9.6	−1.3 (9)

average of all conformations. Earl and Wilson [11] and Neal *et al*. [13] both demonstrated the importance of preferential selection of certain molecular conformations in explaining the observed experimental helical twisting power. Earl and Wilson [11] showed that helix inversion with temperature can be explained by the probability of certain conformers varying with temperature and hence their contribution to the average chirality. Neal *et al*. [13] demonstrated a bimodal distribution of conformers for a TADDOL molecule, with one mode having a very small scaled chiral index and the other a high scaled chiral index. The simulation studies presented here are in the gas phase not the liquid crystal phase where solute–solvent interactions may influence the relative probability of conformations and hence their contribution to the average scaled chiral index. Nevertheless gas phase simulations have provided an explanation of physical properties such as helical twist inversion with temperature.

A molecular dynamics simulation was undertaken in the gas phase for each molecule starting from the optimized conformation to perform a conformational search. The TINKER [22–27] modular programme package was employed to carry out the simulations using the MM3 force field. Augmented parameters from the CACHe programme were utilised together with partial charges from the minimized molecular geometry using the AM1 Hamiltonian. During the simulations chiral constraints were used to ensure that the conformations remained in one enatiomeric form. Table 1 illustrates the average values of the scaled chiral index, $-\langle G_{0S}\rangle \times 10^4$, compared to the experimental values of HTP and the values for the single optimized geometry for each molecule, $-G_{0S} \times 10^4$. The value for the molecule with the sulphur substituents now has the correct sign whilst that of the molecule with more substituents remains the wrong sign. The errors due to the averaging of 15 and 9 are of the order of magnitude of the helical twisting power for this sample of 10,000 conformations. Long simulation runs will be required for single molecules to provide reliable estimators of helical twisting power for dopant molecules with small experimental helical twisting power.

The effect of rotational freedom for methyl and methoxy substituents as a function of separation has proved to be a key feature in the predictive power of the scaled chiral index of helical twisting power. This is the subject of an ongoing extensive study which identifies the effect of scale invariance of the index and the need to employ a cut-off for this type of molecule [28].

4. CONCLUSION

We have undertaken a calculation of a scaled chiral index for two biphenyl molecules with different numbers of substituents that are able to rotate relative to the ring carbons more than the binapthyl and helicene molecules previously considered. One optimized geometry was found for each molecule and the scaled chiral index calculated and found to have the wrong sign for each case. These two molecules were part of a set of eight biphenyl molecules with a range of substituents. The correct sign was predicted by the scaled chiral index for the helical twisting power for six of the biphenyl molecules, not considered here. Since each molecule considered has an accessible set of conformations with very similar energy a simulation study was undertaken for both. The results of the average value of the scaled chiral index from a series of conformations generated by a molecular dynamics simulation were calculated. The correct sign was predicted for one molecule from the conformational average but not for the other. The incorrect sign is linked to substituents with greater rotational freedom. Future work will investigate the effect of a cut-off on conformational averages of the scaled chiral index for the full range of biphenyl molecules and other more flexible ferroelectric liquid crystal molecules. The scale invariance of the index may be causing such methyl and methoxy substituents to contribute in an non-physical manner to the index at large distances so causing the incorrect sign predicted in the helical twisting power.

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