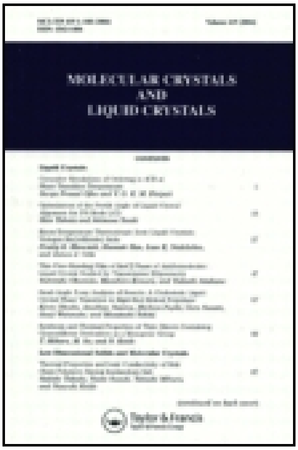

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Similarity and Chirality Measures for Liquid Crystal

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Similarity and Chirality Measures for Liquid Crystal

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The mechanism for the transfer of chirality between a chiral dopant and an achiral liquid crystal host phase remains the subject of conjecture. A review of the theoretical approaches undertaken to create a better understanding of the concept of chirality in liquid crystals proposed a Hausdorff measure of chirality between two enantiomers. We compare this measure with a scaled chiral index. The latter has been successful in predicting the helical twisting power of a range of dopants in nematic solvents but possesses no solvent interaction. We propose a combined measure as a predictive tool for helical twisting power and the for the mechanism for chirality transfer.

Keywords: hausdorff measure; scaled chiral index

1. INTRODUCTION

Following from Lord Kelvin's definition of chirality in 1904 [1] that a chiral object has no mirror symmetry, a range of approaches have been undertaken to quantify chirality. An extensive review has been undertaken by Mislow and co-workers [2] which classified chiral measures into two types; those that measure the difference between a chiral object and a non-chiral reference object and those that measure the extent to which two enantiomorphs differ from one another. There has been little application of the former method. Mislow and co-workers defined a Hausdorff measure of the second kind and applied it to model scalene triangles and tetrahedra. Figgemeier and Hiltrop [3] applied the Hausdorff measure to predict the helical twisting power of a set of oxiranes and thiranes. This application is of interest

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because the molecules have chiral centres and we discuss it here. A third approach to quantifying chirality from molecular structure has led to a range of indices being proposed for example by Nordio and co-workers [4,5,6], Osipov, Pickup and Dunmur [7] and Neal and co-worker [8,9]. These have had a wide applications from chiral dopants [4–6,8–12], to odd even effects [12], biaxial nematics [13], ferroelectrics [14] and chirality of proteins [15,16]. The results for a single optimised geometry for a range of molecules have been surprisingly successful providing evidence that the dopant molecule geometry may be considered to be the major influence upon helical twisting power in some host-dopant interactions. However, the transfer of chirality between a chiral dopant and an achiral liquid crystal host phase remains the subject of conjecture [16]. The extent of the influence of the dopant on the host and the examples where the dopant imparts different degrees of chirality on different hosts demonstrates that the mechanism remains open to question [17]. We present calculations of a scaled chiral index G_{0S}, [7,8], and compare them with the Hausdorff measure $\chi(H)$ [2], both described in section two, and with their ratio. We calculate these measures for a set of oxiranes and thiranes for a single optimized geometry [3]. In section three we compare the calculated results and make comparison with experimental values of relevant helical twisting power values. Conclusions are presented in the final section.

2. SCALED CHIRAL INDEX & HAUSDORFF CHIRALITY MEASURE

An approach which calculates chirality parameters for a molecular structure was proposed by Osipov, Pickup and Dunmur [7]. They defined an isotropic chirality index G_0 for a molecule. 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 [8] for general molecular structures by calculating a scaled chiral index $G_{OS} = \frac{1}{3}\frac{4!}{N^4}$ Go that allows comparison of molecules of different size given by:

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

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 consider. For large molecules such as proteins a cut-off form is required [15,16] but not for the small dopants consider here.

Mislow and co-workers [2] proposed a Hausdorff chirality measure based on overlap of two enantiomers from the Hausdorff distance $H(Q, Q')$ between two sets of points, where Q is the set of coordinates of a chiral molecule and Q' the set of coordinates of its mirror image. They described $H(Q, Q')$ as the smallest number δ that has the following two properties; each spherical ball of radius δ centred at any point of Q contains at least one point of Q' and each spherical ball of radius δ centred at any point of Q$'$ contains at least one point of Q. Then,

$$H(Q, Q') = \max\left[\sup_{q' \in Q'} \delta(Q, q'); \sup_{q \in Q} \delta(Q', q)\right] \tag{2}$$

Mislow and co-workers [2] introduced the Hausdorff chiral measure as

$$\chi^{(H)} = \frac{H_{min}(Q, Q')}{d(Q)} \tag{3}$$

where $H_{min}(Q, Q')$ is minimized by translations and rotations to obtain maximum overlap. The Hausdorff measure is normalized by the spatial extent d(Q) so lies between 0 and 1. It is an absolute chiral measure. Mislow and co-workers conjectured that for this optimal overlap the union of Q and Q$'$ is achiral. We will discuss the implications of this in the next section.

3. CHIRAL OXIRANE & THIRANES DOPANTS

Liquid crystal dopants are used to aid the synthesis of materials with high macroscopic helical twisting power (β) [19] given by:

$$\beta_{\mathcal{M}} = (p\ c_w\ r)^{-1} \tag{4}$$

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. Following Figgemeier and Hiltrop [3] we consider a set of methyl- and phenyl- substituted oxiranes and thiranes in the host MBBA, shown in Figure 1 and Table 1, together with their experimental helical twisting power [20]. The optimized geometry for each 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

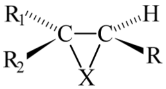

FIGURE 1 Chemical structure of oxiranes and thiranes with substituents shown in Table 1.

given in Table 1. The Hausdorff chiral measures were taken from Figgemeier and Hiltrop [3]. It is apparent that $\chi(H)$ cannot predict the sign as it lies between 0 and 1, by definition. On the other hand the scaled chiral index, $-G_{0S} \times 10^4$, shows a Pearson correlation of 0.81 with the helical twisting power and predicts the sign in 9 of the 11 cases. The Pearson correlation is improved to 0.83 if we compare $-G_{0S} \times 10^4/\chi(H)$ with the experimental HPT as shown in Figure 2 below. This improved correlation demonstrates that $\chi(H)$ shows an inverse relationship with the experimental helical twisting power. In investigating this relationship we found a correlation of 0.87 between the magnitude of the experimental helical twisting power and the Langmuir form of $\alpha/\chi(H)\ (1 + b/\chi(H))$ where $a = 5.0$ and $b = 0.4$. This correlation is far higher than the 0.77 found for the simpler inverse form, $1/\chi(H)$. The form of the Langmuir function describes processes such as adsoption of molecules on a surface or population growth that are tending to a limiting value. Following from the conjecture that $\chi(H)$ is optimized when the non-chiral overlap is a

TABLE 1 Experimental Helical Twisting Powers [20] and calculated chiral measures, $\chi(H)$ and $\chi(H)_{MBBA}$ [3] and $-G_{0S} \times 10^4$ for oxiranes and thiranes in the host phase MBBA (*p*-methoxybenzaylidene *p*-*n*-butylaniline)

Molecule number	R	R1	R2	X	Experimental helical twisting power, βm, [20]	$-G_{0S} \times 10^4$	$\chi(H)$ [3]	$\chi(H)_{\mathrm{MBBA}}$ [3]
1	Ph	Ph	H	O	−35	−40.9	0.085	0.130
2	4-Py	4-Py	H	O	−42	−50.3	0.095	0.130
3	Ph	Ph	H	S	−26	−37.4	0.082	0.130
4	Ph	CH3	H	O	−8.5	41.7	0.105	0.145
5	Ph	PhCO	H	O	−14	−44.1	0.102	0.105
6	*p*-ClPh	PhCO	H	O	− 13.5	−9.7	0.097	0.095
7	Ph	3-ThCO	H	O	−9.5	−13.3	0.102	0.095
8	Ph	H	H	O	−1.2	43.9	0.124	0.185
9	Ph	H	CH_3	O	−0.9	−0.42	0.105	0.145
10	CH3	CH3	H	O	+0.5	49.5	0.162	0.265
11	CH3	CH3	H	S	+0.5	34.2	0.147	0.255

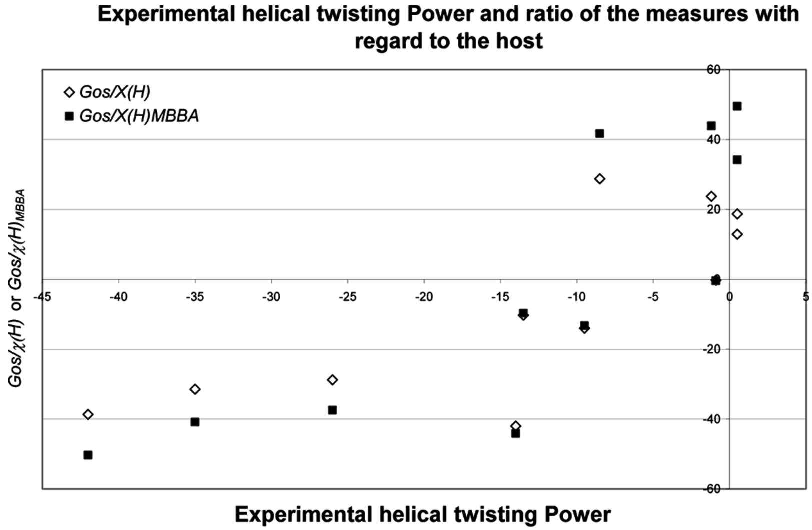

FIGURE 2 Ratio of scaled chiral index to Hausdorff measure and to Hausdorff measure with regard to MBBA for some substituted oxiranes and thiranes in MBBA. HTP data, see [20] and Hausdorff data see [3].

maximum we put forward the conjecture that the mechanism of chiral transfer is determined by the non-overlap chiral region since the induced helical twisting power increases proportional to the limit approached by the inverse form of the Hausdorff measure. The Hausdorff measure can be used to compare the overlap of a dopant and host as well as a dopant and its enantiomer and Figgemeier and Hiltrop [3] also calculated this Hausdorff measure, $\chi(H)_{MBBA}$. The correlation between helical twisting power and $G_{0S}/((\alpha/\chi(H)_{MBBA})/((1+b)/\chi(H)_{MBBA}))$ is 0.81. This is an improvement on the correlation of 0.79 using the same form but for $\chi(H)$ instead of $\chi(H)_{MBBA}$, giving an indication of $\chi(H)_{MBBA}$ low level dopant host interaction.

4. CONCLUSION

We have undertaken calculations of a scaled chiral index for a set of minimized structures of oxiranes and thiranes. We have compared the correlation between the experimental helical twisting power and that predicted by the scaled chiral index and by the Hausdorff chirality measure. For the latter measure we used the results of Figgemeier and Hiltrop. We have found an approximate inverse relationship between χ(H) and the magnitude of the helical twisting power and a high

Pearson correlation of 0.87 between the Langmuir form for $(G_{OS})/((\alpha/\chi(H))/(1+b)/(\chi(H)))$ and the magnitude of the helical twisting power. We have made the conjecture that the chiral non-union of the dopant and the host determines the chirality transfer mechanism We have shown that either $-G_{0S}\times 10^4/\chi(H)$ or $G_{OS}/((\alpha/\chi(H)_{MBBA})/((1+b)/\chi(H)_{MBBA}))$ improves the prediction of the experimental helical twisting power compared to $-\mathrm{G}_{0S}\times 10^4$ aloneand can be utilised to investigate if the induced helical twisting power is affected by a host dopant interaction as is sometimes the case.

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