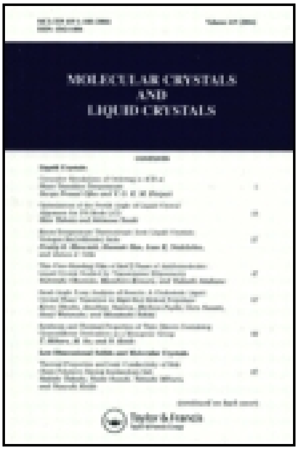

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Non-Traceless Molecular Pseudotensor for a Description of the HTP

H.-G. Kuball [a], O. Türk [a], I. Kiesewalter [a] & E. Dorr [a]

[a] FB Chemie, Universität Kaiserslautern, D-67653, Kaiserslautern, Germany

To cite this article: H.-G. Kuball, O. Türk, I. Kiesewalter & E. Dorr (2000): A Non-Traceless Molecular Pseudotensor for a Description of the HTP, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 352:1, 195-204

To link to this article: http://dx.doi.org/10.1080/10587250008023177

Mol. Cryst. and Liq. Cryst., 2000, Vol. 352, pp. 195-204
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A Non-Traceless Molecular Pseudotensor for a Description of the HTP

H.-G. KUBALL, O. TÜRK, I. KIESEWALTER and E. DORR

FB Chemie, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany

For a description of the HTP with quantities determined by structural elements of a molecule, the chirality interaction tensor $\underline{\underline{W}}$ has been introduced. The diagonal elements of $\underline{\underline{W}}$ with respect to the principal axes of the order tensor of some unbridged 1,1′-binaphthyls have been determined from the temperature dependence of the HTP and that of the order tensor. The distinct smaller W^*_{ii} (i=1,2,3) of unbridged 1,1′-binaphthyls in comparison to those of bridged 1,1′-binaphthyls can be explained as a result of an ordering phenomenon originated by the large amplitude motion about the dihedral angle φ of the naphthyl-naphthyl bond. There is no necessity to assume a chiral zero for the diagonal elements of $\underline{\underline{W}}$ for conformers with a dihedral angle between $0° \leq \varphi \leq 180°$.

Keywords: Helical Twisting Power; exciton chirality; 1,1′-binaphthyls; order tensor; chirality interaction tensor

INTRODUCTION AND BASIC EQUATIONS

Chiral molecules dissolved in a chiral or achiral liquid crystal host phase map their chirality onto the phase developing or varying a supramolecular chirality in the phase given by a chiral long-range positional and orientational order. In cases where the chiral structure is of helical order, the reciprocal pitch or its derivative with respect to the mole fraction of the guest x_e are suitable quantities for a quantitative description of the chiral induction. But these quantities are not symmetry adapted for chiral guests in chiral liquid crystalline hosts. Thus, a sum and a difference of the derivatives with respect to the mole fractions of the enantiomers are necessary for the pseudoscalar helical twisting power (HTP; upper sign) and the achiral part of the induction, the scalar achiral helical twisting power (AHTP; lower sign) [1]:

$$(\mathrm{HTP})_e = \frac{1}{2}\left\{\left(\frac{\partial p^{-1}}{\partial x_e}\right)_{x_e=0} \mp \left(\frac{\partial p^{-1}}{\partial x_{e^\dagger}}\right)_{x_{e^\dagger}=0}\right\}. \qquad (1)$$

$e^\dagger$ denotes the enantiomer of e and x_e, $x_{e\dagger}$ are the mole fractions of e and $e^\dagger$, respectively. For an achiral host phase $\left(\frac{\partial p^{-1}}{\partial x_e}\right)_{x_e=0} = -\left(\frac{\partial p^{-1}}{\partial x_{e^\dagger}}\right)_{x_{e^\dagger}=0}$, it follows

$$(\mathrm{HTP})_e = \left(\frac{\partial p^{-1}}{\partial x_e}\right)_{x_e=0} = -\,(\mathrm{HTP})_{e^\dagger} = \sum_i x_{e,i}(\mathrm{HTP})_{e,i}, \qquad (2)$$

where the AHTP of the guest is equal to zero. The HTP and also the AHTP depend on the composition of the host system. For dilute solutions of a chiral guest the HTP is a linear function of the mole fractions of possible guest conformers $x_{c,i}$.

For a structure/response relation the question arises which properties of the structure of a chiral compound are the basis for a description of the chiral induction. From the theoretical point of view three findings are of importance: 1) The HTP can possibly be described by a pseudoscalar quantity [2]. 2) The HTP can be successfully described by a traceless helicity tensor [3] describing the "form chirality" of a molecule which is mapped onto the host phase by an alignment of the host molecules on the surface of the guest molecules. 3). The HTP depends strongly on the orientation of the principal axes of the order tensor with respect to the skeleton of the chiral guest molecules [1]. The representations of de Gennes [2] and Nordio et al. [3] seem contradictory. De Gennes's description introduces a pseudoscalar quantity by which the chiral induction is independent of the orientation of the guest with respect to the local director of the host. With the description of Nordio et al. the HTP will tend to zero if the chiral guest is isotropically distributed in the ordered host phase. Both approaches can be seen as limiting cases of a description with a non-traceless chirality interaction tensor $\underline{\underline{W}}$, a pseudotensor of second rank which can be introduced by a contraction of a chirality tensor of the guest C_{ij} and a tensor L_{ij} representing host phase properties: $W_{ij} = \sum_k C_{ik}L_{kj}$. $W = \mathrm{Tr}\ \{W_{ij}\} \neq 0$ corresponds to de Gennes's pseudoscalar quantity [4]:

$$\mathrm{HTP} = \sum_{i=1}^{3} g^{*}_{ii33}\, W^{*}_{ii} = \frac{1}{3}W + \left(W^{*}_{33} - \frac{1}{3}W\right)S^{*} + \frac{1}{\sqrt{3}}\left(W^{*}_{22} - W^{*}_{11}\right)D^{*}. \quad (3)$$

The $g_{ijkl} = \frac{1}{8\pi^2}\int f(\Omega)\, a_{ik}(\Omega)\, a_{jl}(\Omega)\, d\Omega$ are the orientational distribution coefficients of the guest in the molecular ensemble of the guest/host phase. $\Omega \equiv \alpha, \beta, \gamma$ are the Eulerian angles and $a_{ij}(\alpha, \beta, \gamma)$ the elements of the transformation matrix from the space-fixed to the molecule-fixed coordinate system. The W^{*}_{ii} are given with respect to the principal axes of the order tensor g_{ij33} in order to avoid non-diagonal elements in eq. (3). The order tensor is correlated to Saupe's order parameters S^{*} and D^{*} by $S^{*} = \frac{1}{2}\left(3g^{*}_{3333} - 1\right)$ and $D^{*} = \frac{\sqrt{3}}{2}\left(g^{*}_{2233} - g^{*}_{1133}\right)$. Eq. (3) resembles the equation for the circular dichroism (CD) of oriented molecules, i.e. the CD of anisotropic samples (ACD), for which the W_{ij} have to be substituted by the circular dichroism tensor: $W_{ij} \to \Delta\varepsilon_{ij}$ [5]. The HTP of unbridged 1,1′-binaphthyls will be analyzed by eq. (3) which has been successfully applied for the description of bridged 1,1′-binaphthyls. Especially the binaphthyls have been chosen to verify eq. (3) because this class of compounds has been studied intensively [6].

EXPERIMENTALS AND RESULTS

The HTP (fig. 1) has been measured with a modified Cano method [7] in a concentration region for which the linear concentration dependency of eq. (2) is valid ($c < 1\%$ of weight). The size of symbols in fig. 1 for the measured points indicates the experimental error. The $\bar{\nu}_{1\text{extr}} < \bar{\nu}_{2\text{extr}}$ are the wavenumbers of the extrema of the bisignate curve, the CD couplet, in fig. 2a. The amplitude of the couplet $\Delta\Delta\varepsilon = \Delta\varepsilon(\bar{\nu}_{1\text{extr}}) - \Delta\varepsilon(\bar{\nu}_{2\text{extr}})$ of the unbridged 1,1′-binaphthyls is about 50 to 60 % of that of the bridged 1,1′-binaphthyls whereas there is a larger decrease and even a sign change of the HTP values of the unbridged 1,1′-binaphthyls. This decrease of the amplitude of the CD couplet is an effect of the smaller splitting of the exciton excited states and because the CD of the decomposed exciton bands A → A and A → B are about 40% smaller than those of the bridged 1,1′-binaphthyls.

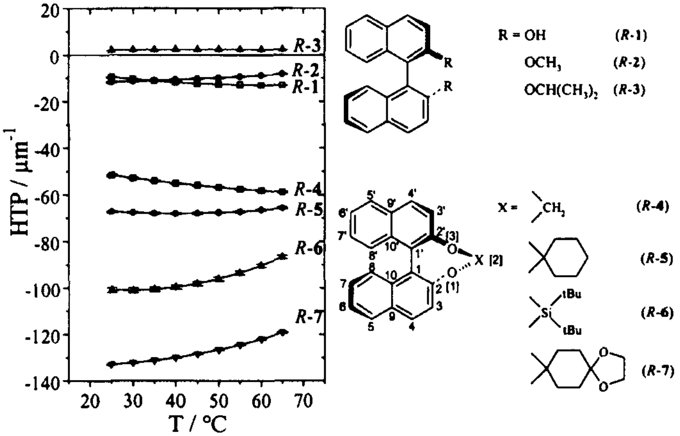

FIGURE 1 The HTP of *R*-1 to *R*-7 in ZLI-1695 (Merck) as a function of temperature.

Also the variation of the amplitude of the couplets of *R*-**1** to *R*-**7** with temperature is smaller than 8 % between 25°C to 65°C for the bridged and the unbridged 1,1'-binaphthyls which is strictly speaking no hint for conformers of *R*-**1** to *R*-**3**. The larger splitting of the UV bands of A → A and A → B for *R*-**4** to *R*-**7** than for *R*-**1** to *R*-**3** as shown by the shoulders (fig. 2b) leads to the conclusion, supported by the potential curves given in fig. 3a, that the interaction between both naphthyl groups is smaller for *R*-**1** to *R*-**3** than for *R*-**4** to *R*-**7** because of a larger dihedral angle φ for the unbridged compounds.

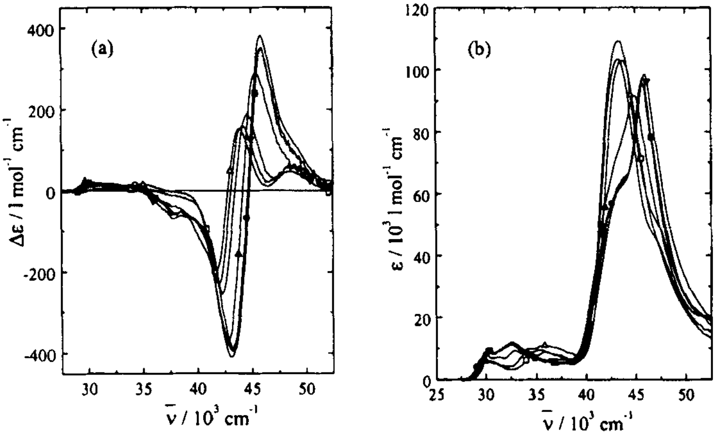

FIGURE 2 CD spectra (a) and UV spectra (b) of the ^1B_b transition of *R*-**1** (□), *R*-**2** (○), *R*-**3** (△), *R*-**4** (■), *R*-**5** (●), *R*-**6** (▲), *R*-**7** (▼) in ZLI-1695 (Merck) at T = 80°C.

DISCUSSIONS

From the temperature dependence of the HTP (fig. 1) and the coordinates of the order tensor determined by ^{2}H NMR [5], the diagonal elements of the chirality interaction tensor have been calculated (tab. 1) with the help of eq. (3). Hereby, eq. (3) means that the projection of the coordinates W_{ij} onto the principal axes of the order tensor W_{ii}^* determines the value of the HTP. As discussed earlier [4] for the bridged compounds *R*-**4** to *R*-**7** the coordinate W_{ii}^*, belonging to the principal axis parallel to the C_2 symmetry axis, yields the main contribution to the HTP. The cisoid arrangement of both naphthyl groups is thus responsible for the sign of the HTP but also for the negative amplitude of the $\Delta\Delta\varepsilon$ of the CD couplet (fig. 2a). The unbridged 1,1'-binaphthyls do not fit into the scheme of the bridged 1,1'-binaphthyls (tab. 1). The dihedral angle estimated from the size of the CD couplet of the bridged 1,1′-binaphthyls is similar to those of the cisoid bridged 1,1′-binaphthyls. If this estimated dihedral angle φ is responsible for the HTP of the unbridged 1,1'-binaphthyls an HTP value similar to that of the bridged 1,1'-binaphthyls should be expected what is in contrast to the experimental findings. The splitting of the UV bands for the unbridged 1,1'-binaphthyls (fig. 2b) and the potential curve calculated by the AM1 method (fig. 3a) predict a larger φ. Furthermore, the flat potential curve from an AM1 calculation for φ about 90° ± 30° (energy variation < kT) in the gas phase allows a Large-Amplitude-Motion (LAM) [8] which is confirmed by the analysis of crystal structures.

TABLE 1 Coordinates of the order tensor[*] for T = 45°C. The HTP in ZLI-1695 and the coordinates of the chirality interaction tensor W^{*}_{11}, W^{*}_{22} and W^{*}_{33} with respect to the principal axes[†] of the order tensor for a constant host order.

Compound	g^{*}_{2233}	g^{*}_{3333}	HTP/ μm^{-1} exp.	W^{*}_{11}	W^{*}_{22}	W^{*}_{33}
R-**1**	0.270	0.620	-12.3	36	-73	5.7
R-**2**	---	---	-10.3	---	---	---
R-**3**	0.305	0.551	2.31	-5.6	14	-2.1
R-**4**	0.381	0.517	-56.0	-1	-202	41
R-**5**	0.401	0.492	-68.0	13	-207	28
R-**6**	0.432	0.438	-98.2	46	-202	-37
R-**7**	0.366	0.523	-128.5	-63	19	-246

For *R*-**1** to *R*-**3** and other compounds described in the literature an angle φ [8, 9] between 65° and 115° has been found in contrast to angles of about 50° to 60° for bridged compounds. Thus, differently solvated conformers with a large angular distribution of φ about the equilibrium angle φ_0 (fig. 3a) can be expected, i.e. the LAM-structure allows solvent stabilized conformers. The HTP of *R*-**1** and *R*-**3** is mainly determined by the term $g^{*}_{2233}W^{*}_{22}$. The order parameters for the different solvent stabilized conformers of *R*-**1** to *R*-**3** in the cisoid and transoid forms should be very different comparing their length to breadth ratio.

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[*] The order tensor of **2** is not measurable because of its insufficient solubility in ZLI-1695.

[†] The numbering of the principal axes of the order tensor is given by the convention: $g^{*}_{3333} \geq g^{*}_{2233} \geq g^{*}_{1133}$.

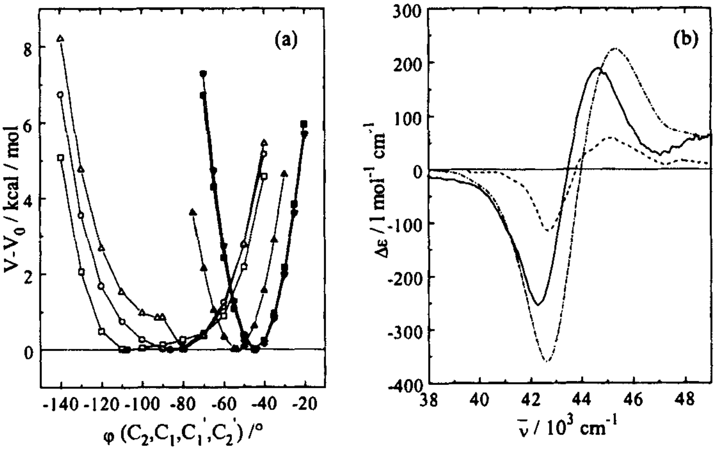

FIGURE 3 (a) Potential curves V-V$_0$ for *R*-**1** (□), *R*-**2** (O), *R*-**3** (Δ), *R*-**4** (■), *R*-**5** (●), *R*-**6** (▲), *R*-**7** (▼) calculated by AM1. (b) CD spectra of *R*-**1** measured in n-heptane at T=25°C (—), calculated by exciton theory as a mean of all conformations weighted by a Boltzmann factor (---), and for the conformer corresponding to the minimum of the potential curve (----).

Assuming that the W_{ii}^{*} are nearly constant over a large interval of φ and do not change their sign, the decreasing values of *R*-**1** can be understood by the weighted mean value of $g_{ii33}^{*}(\varphi)\, W_{ii}^{*}(\varphi)$. Also a sign change seems possible. The CD spectrum is the concentration-weighted mean of the Δε of all conformations, and thus leads to a couplet comparable to that of the bridged 1,1'-binaphthyls because in this case the mean value of the couplet is a mean over positive and negative couplets where the size of the positive couplets of the transoid forms are smaller than the negative couplets of the cisoid forms. This conclusion is confirmed with a CNDO/S-CI and a exciton coupling calculation which gives a fair agreement with the experimental spectrum (fig. 3b).

ACKNOWLEDGEMENT

Financial support form the "Deutsche Forschungsgemeinschaft", the "Volkswagen Stiftung", and the "Fonds der Chemischen Industrie" is gratefully acknowledged.

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