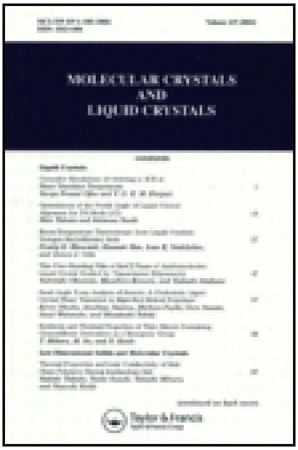

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The Chiral Induction of Chiral Nematics and the Anisotropic Circular Dichroism

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The anisotropic circular dichroism (ACD) and the chiral induction (HTP) are two chirality measurements of very different kind. For two binaphthyls diagonal elements of the circular dichroism (CD) tensor have been determined from the temperature dependence of the ACD and diagonal elements of the chirality interaction tensor from the temperature dependence of the HTP as a function of the order parameters. The tensor coordinate of the CD tensor and the chirality interaction tensor which belongs to the direction along the naphthyl-naphtyl bond determines mainly the ACD and HTP, respectively. In both cases an order independent contribution to the ACD and HTP exist.

Keywords: Helical twisting power; chirality interaction tensor; anisotropic circular dichroism; circular dichroism tensor; 1,1′-binaphthyls

INTRODUCTION AND BASIC EQUATIONS

The macroscopic anisotropy of an achiral or a chiral phase is determined by the anisotropy of the molecules and their anisotropic ordering. The chirality of a chiral nematic is originated by the chirality of the molecules and the chirality of long-range orientational order in the phase, the suprastructural chirality [1]. The results of two chirality measurements of chiral anisotropic systems of very different type will be compared: the anisotropy of circular dichroism (ACD, $\Delta\varepsilon^A$) which yields information about the interaction of light with individual molecules [2] and the chiral induction (HTP) which has its origin in the interaction of chiral and achiral molecules [3]. In spite of the fact that the ACD is mainly a molecular property and the HTP an effect of the chiral dopant and of phase properties, the question can be raised which common conclusions can be drawn for the intermolecular chirality transfer because both effects can be traced back to the dopant's chirality.

The circular dichroism (CD) is the different absorption of two independent eigenstates of light, i.e., of left (L) and right (R) circularly polarized light, propagating, e.g., along the optical axis of a uniaxial phase. There are two pieces of information from the molar decadic absorption coefficients ε_L and ε_R. The chirality measurement, the ellipticity $\theta = \ln 10 * (\varepsilon_L - \varepsilon_R)cd$ with $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$, the circular dichroism, and the mean absorption $\bar{\varepsilon} = (\varepsilon_L + \varepsilon_R)/2$ which is not a chirality measurement. For the chiral induction of chiral phases analogous equations can be obtained [3,4]. For the chirality measurement follows:

$$(\mathrm{HTP})_e = \frac{1}{2}\left\{\left(\frac{\partial p^{-1}}{\partial x_e}\right)_{x_e} - \left(\frac{\partial p^{-1}}{\partial x_{e^+}}\right)_{x_{e^+}}\right\}, \tag{1}$$

where x_e is the mole fraction of the chiral dopant e. e^+ denotes the enantiomer of e. With only one chiral compound in the phase the following relation holds for $x \ll 1$:

$$\left(\frac{\partial p^{-1}}{\partial x_e}\right)_{x_e} = -\left(\frac{\partial p^{-1}}{\partial x_{e^+}}\right)_{x_{e^+}} = \mathrm{HTP} = \sum_i x_i (\mathrm{HTP})_i \tag{2}$$

The relations between the circular dichroism tensor $\Delta\varepsilon_{ij}$ and the ACD ($\Delta\varepsilon^A$) and the chirality interaction tensor W_{ij} and the HTP are of the same structure (eq. (3)) for a situation schematically shown in fig. 1. Here, the measurement of the anisotropic circular dichroism means a CD measurement with a light beam propagating along the optical axis of a uniaxial phase without suprastructural chirality. With $M_{kl} = \sum_{i,j} g_{ijkl} X_{ij}$ and $M_{33} = \Delta\varepsilon^A$ or $M_{33} = \mathrm{HTP}$ and the coordinates of order tensor g_{ijkl} (k, l = 1,2,3) then follows for the ACD and for the HTP [2,3,4]

$$M_{33} = X^*_{11} + \left(X^*_{22} - X^*_{11}\right) g^*_{2233} + \left(X^*_{33} - X^*_{11}\right) g^*_{3333} \tag{3}$$

with $X_{ij} = \Delta\varepsilon_{ij}$ and $X = 3\Delta\varepsilon = \sum_i \Delta\varepsilon^*_{ii}$, the circular dichroism, or with $X_{ij} = W_{ij}$ and $W = \sum_i W^*_{ii}$, the chirality interaction tensor. $\Delta\varepsilon$ and W are pseudoscalar molecular quantities measured for a chiral molecule by ACD and HTP, respectively. Eq. 3 can be rewritten also with $S^* = (3g^*_{3333} - 1)/2$ and $D^* = \sqrt{3}(g^*_{2233} - g^*_{1133})/2$. Eq. (3) for the HTP is a generalization of an equation given by Nordio et al. [5]. Whereas for the CD or ACD eq. (3) is correct in its order of approximation, two further terms depending on two additional order parameters are needed [6] for a locally biaxial cholesteric phase of symmetry D_2 built up by chiral dopants of a symmetry or effective symmetry of point symmetry group D_2. There is still no possibility to estimate their effect and to determine the additional order parameters.

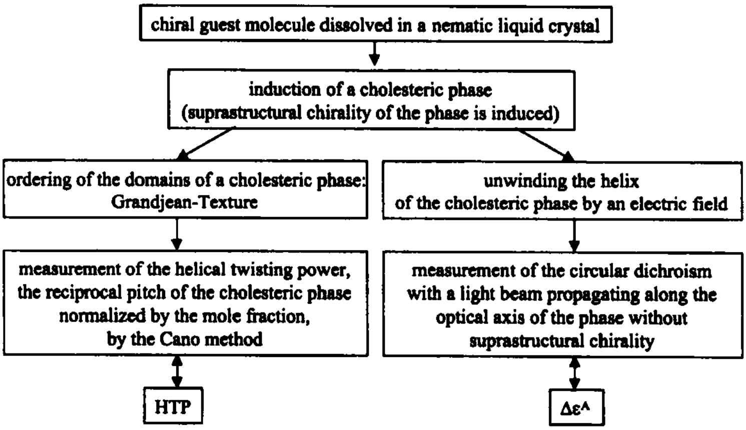

FIGURE 1 Experimental conditions for the HTP and ACD.

EXPERIMENTALS AND RESULTS

The order tensor of the binaphthyls *R*-**1** and *R*-**2** (fig. 3) has been measured by ^{2}H NMR, the order tensor of the host phase by ^{13}C NMR [7]. Fig. 2 shows also $D^* = f(S^*, \delta)$ [8] with $\delta = 0{,}85$ for *R*-**1** (left curve) and $\delta = 1{,}00$ for *R*-**2** (right curve) which allows an extrapolation of the order of the dopant to $S^* = 0$ and 1. The HTP curves for *R*-**1** and *R*-**2** (fig. 2 left) measured in two liquid crystal phases show that the twist constant K_{22} cannot influence the HTP simply as a reciprocal factor, as e.g. shown by Nordio, because the ratio HTP_{ZLI} / HTP_{K15} is different for both compounds. The CD in the isotropic solution of *R*-**1** and *R*-**2** is equal within the experimental error (fig. 3). The ACD for *R*-**1** and *R*-**2** is different (fig. 3) because of the different order in the phase (fig. 2.) as shown in fig. 4 where the change and its consequence is vizualized.

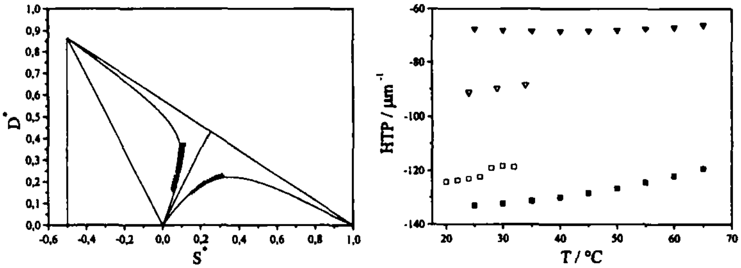

FIGURE 2 Order parameters of *R*-**1** (▼) and *R*-**2** (+) in ZLI-1695 (Merck, Darmstadt) given with respect to the principal axes of the order tensor of *R*-**2** (+) (left); the HTP (right) of the binaphthyls *R*-**1** (▼) and *R*-**2** (■) in ZLI-1695 (Merck) and in K-15 (Merck, ∇,□) as a function of temperature, respectively.

By looking along the orientation axis (x_3^*) of *R*-**1** (fig. 4, (1)) and of *R*-**2** (fig. 4, (2)) the orientational distribution about the two x_3^* axes is expected to be changed due to the structural anisotropy and thus D^* should be changed which is confirmed experimentally (fig. 2). This variation of the orientational distribution as a function of the variation of the substituent R can be followed by proceeding along the idealized curves in fig 2.

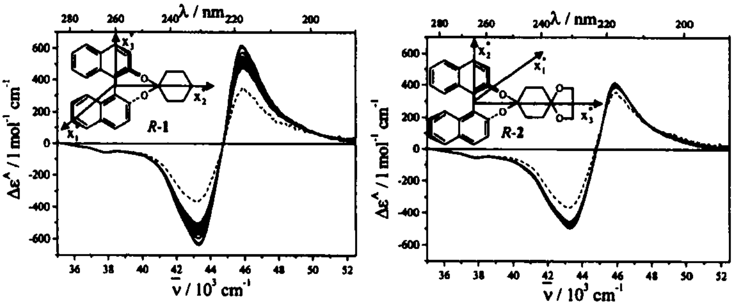

FIGURE 3. $\Delta\varepsilon^A$ of *R*-1 (left) and of *R*-2 (right) in ZLI-1695 (Merck) for $T^* = 0,89$ to $0,99$ from above at $\bar{\nu} = 45977$ cm^{-1}. $\Delta\varepsilon$ (.......) is the CD of the isotropic phase at T= 72°C.

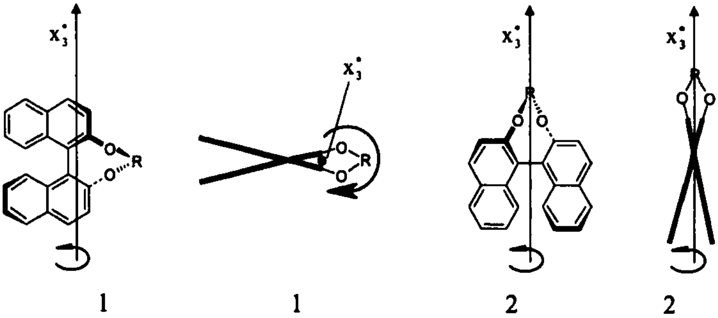

FIGURE 4 Two different orientational distributions induced by variation of the substituent R.

The determination of the coordinates of the CD tensor obtained by fitting the ACD as a function of the order parameters only gives, e.g., $\Delta\varepsilon_{33}^*$ and $\Delta\varepsilon_{11}^* + \varepsilon_{22}^*$ in a good approximation because of the large errors in D^*. The assumption that the CD tensor coordinates of *R*-1 and *R*-2 are equal allows the determination of all CD tensor coordinates (fig. 5) which are consistent with the data for $\Delta\varepsilon_{33}^*$, $\Delta\varepsilon_{11}^* + \varepsilon_{22}^*$ given above. The evaluation of W_{ij} suffers from the fact that its temperature dependence is not known. W_{ij} can be strongly influenced by properties of the host phase.

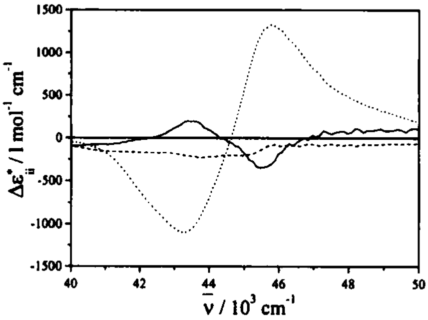

FIGURE 5 The diagonal elements of the CD tensor of *R*-**1** ($\Delta\varepsilon^*_{11}$ (—), $\Delta\varepsilon^*_{22}$ (····), $\Delta\varepsilon^*_{33}$ (—)) and *R*-**2** ($\Delta\varepsilon^*_{11}$ (—), $\Delta\varepsilon^*_{22}$ (——), $\Delta\varepsilon^*_{33}$ (····)) with respect to their own principal axes (fig. 3).

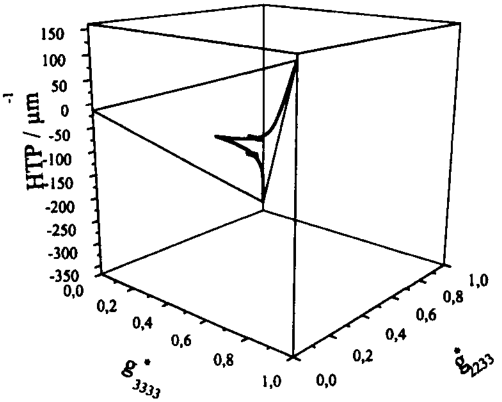

FIGURE 6 The plane HTP = HTP (g^*_{3333}, g^*_{2233}) for *R*-**1** (lower points; δ = 1,00) and *R*-**2** (upper points; δ = 0,85) according to eq. (3) with (W^*_{11}, W^*_{22}, W^*_{33}) = (-14,- 348,150) / µm^{-1} [9].

There is a possibility to check this influence by using the fact that eq. (3) describes a plane in the (g^*_{3333}, g^*_{2233}, HTP) "space" [9] if W_{ij} is temperature independent (fig 6). Temperature dependent W_{ij} and $\Delta\varepsilon_{ij}$ would yield experimental points which are not in the plane. Because this is not found for *R*-1 and *R*-2 this is a strong hint that W_{ij} is approximately temperature independent. Fitting the plane allows the determination of the diagonal elements of W_{ij} (legend of fig. 5) with respect to the principal axes of the order tensor by the S*, D* (g_{2233}, g_{3333}) dependence. The conclusion is that for the different chirality measurements, $\Delta\varepsilon^A$ and HTP, the coordinates of different eigendirections of the same structural elements are important and that the trace of W_{ij}, the order parameter independent contribution, is important for size and sign of the HTP of *R*-1 and *R*-2.

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References

[1] H.-G. Kuball, *Liquid Crystals Today*, **9**, 1-7 (1999).
[2] H.-G. Kuball, T. Höfer in K. Nakanishi, N. Berova, R.W. Woody, eds., *Circular Dichroism: Principles and Applications* John Wiley & Sons, New York, p. 133, 2000.
[3] H.-G. Kuball, H. Brüning, *Chirality*, **9**, 407 (1997).
[4] H.-G. Kuball, O. Türk, *Polish J. Chem.*, **73**, 209 (1999).
[5] A. Ferrarini, G.J. Moro, P.L. Nordio, *Mol. Phys.*, **87**, 485 (1996).
[6] H.-G. Kuball, E. Dorr in D. A. Dunmur, A. Fukuda, G. R. Luckhurst, eds., *Physical Properties of Liquid Crystals, Vol. 1: Nematics*, IEE, Stevenage, UK, in press 2000.
[7] I. Kiesewalter Dissertation University of Kaiserslautern 1999.
[8] G.R. Luckhurst, C. Zannoni, P.L. Nordio, and U. Segre, *Mol. Phys.*, **30**, 1345 (1975).
[9] T. Höfer, Dissertation University of Kaiserslautern 2000.