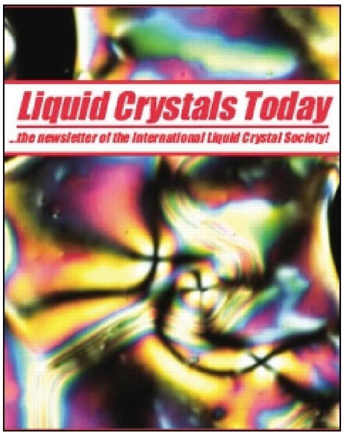

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From Chiral Molecules to Chiral Phases[1]: Comments on the Chirality of Liquid Crystalline Phases

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From chiral molecules to chiral phases[1]: Comments on the chirality of liquid crystalline phases

In this issue:

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In liquid crystal science the phenomenon of chirality has often played an important role in the context of phase structures or as an origin of symmetry breaking. Fundamental questions about 'chirality' in the context of liquid crystal properties have not been widely discussed or taken into account in the development of suitable concepts. For example, the questions of whether or not the spontaneous polarization or the circular dichroism (CD) with a light beam propagating obliquely to the optical axis of the phase is a chirality observation, have never been asked. With the report in 1996 of chiral liquid crystal phases [1], formed from achiral 'banana-shaped compounds', a new era of discussion dawned. Many questions are now raised which seem to be trivial, but are also fundamental, e.g. can a commercial CD instrument measure CD of an anisotropic and inhomogeneous phase without artifacts or whether or not a measured CD is an unequivocal proof for the existence of a chiral structure.

What is chirality?

Chiral objects can be of very different kinds and exist in very different time domains. In the following the discussion will be restricted to geometrical objects for which Lord Kelvin [2] gave in his Baltimore lectures 1884 the following successful definition: *'I call any geometrical figure or group of points 'chiral', and say it has 'chirality', if its image in a plane mirror, ideally realized, cannot be brought[2] into coincidence with itself'*. The definition given neither provides a method to prove the existence of chirality nor describes a procedure for its measurement. Here, chirality exists as a phenomenon of symmetry and not as a quantitative measure.

When an anisotropic object possessing an internal structure is mirrored, not only its internal structure but also the position and the orientation of the mirror image of the object in space is altered in comparison to its initial situation. If the object is an anisotropic phase with an internal structure built up from molecules, the microscopic positional and orientational order of all individual molecules of the ensemble will in general also be altered. It then seems hopeless to find a procedure of superimposing the image and mirror image of the system. Obviously Kelvin's definition cannot be applied simultaneously to the external and internal structure without problems, except for a homogeneous isotropic phase where for every object, i.e. every molecule in a homogeneous medium, a molecule in the mirror image situation of orientational and positional order is present. To avoid such problems, only individual objects should be considered at one and the same time. Then an object is chiral if and only if it possesses no symmetry operation of the second kind, i.e. no rotation reflection axis S_n. With this procedure objects, including molecules, can be classified

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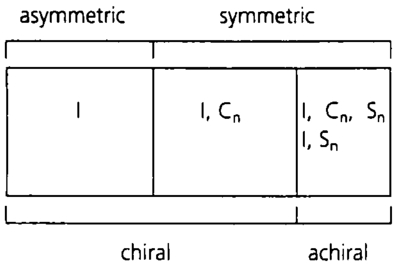
[1] Excerpt from a lecture given at the *27. Freiburger Arbeitstagung Flüssige Kristalle* from 25th to 27th of March 1998.

[2] By rotation and translation of the geometrical figure or the group of points.

(continued on page 2)



in three classes, as shown above, where *I* is the identity operation and C_n represents an *n*-fold rotation axis.

For complex systems like convoluted polymers or dynamic systems like liquid crystal phases or objects which change their structure with time by a fluctuation of orientational and/or positional order, an extension of Kelvin's definition has been obtained by introducing a measure of chirality [3]: *'Chirality is the inability to make a structure coincide with a statistical realization of its mirror image; the probe-dependent measure of this inability is the chirality content C of the structure'.* Instead of the statement that a system is chiral or not, one has to ask how chiral the system is. The chirality content of an object is then given by the measure

$$C = \sum_i \left\| P_i^2 - \hat{P}_i^2 \right\|, \qquad (1)$$

with $0 \leq C \leq 1$, which compares the positions of the points (atoms) P_i of the image with the points $\hat{P}_i$ of the mirror image. C is only zero for an achiral system. $C = 1$ means chiral in a maximal way. The drawback of such an extension is the necessity to introduce some kind of quantitative measure of chirality.

The four levels of chirality

To overcome the problem with chiral phases possessing an internal structure, four different structural levels can be considered which are formed by (1) the atoms, (2) the molecules, (3) the internal structure of a phase and (4) the form or shape of a macroscopic object. With

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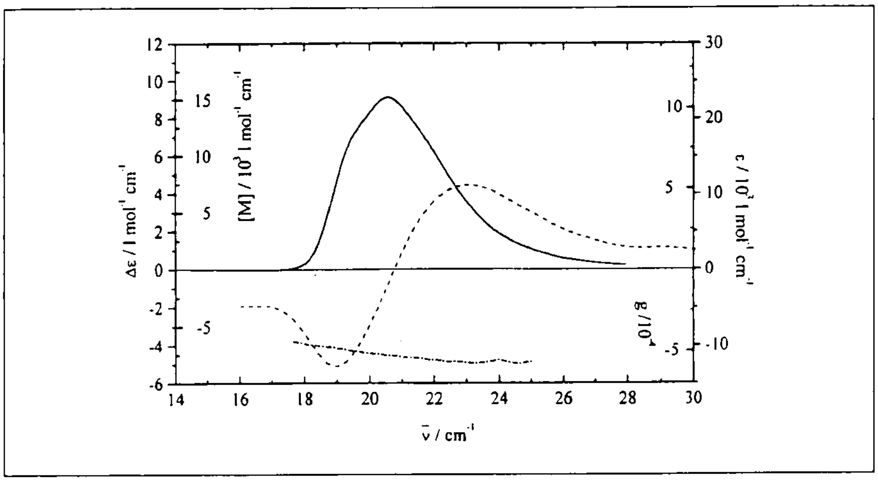

Figure 1. Schematic representation of the UV absorption (ε), the CD ($\Delta\varepsilon = \varepsilon_L - \varepsilon_R$), and the ORD ($[M] \approx n_L - n_R$), i.e. the Cotton effect in a UV absorption region. ε_L, ε_R and n_L, n_R are the molar decadic absorption coefficients and the refractive indices for left and right circularly polarized light, respectively. g is the dissymmetry factor which on one hand characterizes chromophores and on the other hand denotes the measurability of the CD and ORD.

each of the four structural elements, chirality can be introduced into a system. The chirality of the atoms originates from the weak interaction forces (first level), that of the molecules (second level) by the fixed arrangements of atoms. The third level of chirality, the 'suprastructural chirality' [4], is formed by long-range positional and long-range orientational order of atoms or molecules in anisotropic phases or through short-range order in isotropic phases. The fourth level of chirality is given by the form of a macroscopic object.

Except in the case of atoms, Kelvin's procedure can be applied to each level separately. How the chirality of different levels can be made comparable or can be correlated is an unanswered question because they are of different kinds. The concepts *chirality observation, chirality measurements, chirality functions and parameters and chirality measure* will now be introduced to facilitate further discussion.

Concepts of chirality

Chirality Observation

A measurement which answers the question whether or not an object is chiral with yes or no is named a *chirality observation*. Well known examples are the circular dichroism (CD) and the optical rotatory dispersion (ORD) (figure 1). A chirality observation can consist of one or more than one measurement. This is demonstrated in figure 2, where a crystal and its mirror image are shown in different orientations. It can be seen immediately that more than one view is necessary to decide whether this 'achiral' object is chiral or not. The number of views required for an unequivocal decision depends on the anisotropy of the object and can only be reduced by some knowledge about the object. For an isotropic chiral solution, a so-called dissymmetric phase, one measurement is sufficient. For uniaxial and biaxial chiral phases with a suprastructural chirality more measurements are required. As an example, the optical rotation and the ellipticity as a function of the azimuth of the sample for different directions of propagation of light can be measured.

Chirality measurements with chiral isotropic and chiral anisotropic phases

With a measurement of a property connected with the chirality of a phase, a *chirality measurement*, values are obtained which distinguish both enantiomeric or enantiomorphic forms of an object. For isotropic systems Ruch and Schönhofer [5] have defined: *'a chirality measurement of a property is a measurement with an ensemble of non-oriented molecules which leads for enantiomers to a result of the same absolute value but with an opposite sign'*. In some improbable situations the measured values can be zero whereas for achiral systems the result of the chirality measurement has to be zero in any case.

Anisotropic phases can be chiral because of the chirality of molecules or a chiral positional and/or orientational order in the phase. Information about the chirality of the anisotropic phases (objects) can be obtained, in principle, from a measurement of an isotropic distribution of an ensemble of such chiral anisotropic phases (objects) which can be conceived as a 'supermolecule'. Then *'a chirality measurement of a property of an ensemble of orientationally and positionally ordered molecules, i.e. of a chiral anisotropic phase, is a measurement of a property of an ensemble of non-oriented 'anisotropic phases', which leads for an enantiomer of the 'chiral anisotropic 'phase' to a result of the same absolute value but with an opposite sign'*. To realize an optical measurement either a direct measurement with an ensemble of isotropic distributed 'supermolecules' has to be performed or the state of polarization of light has to be measured with light beams penetrating the anisotropic

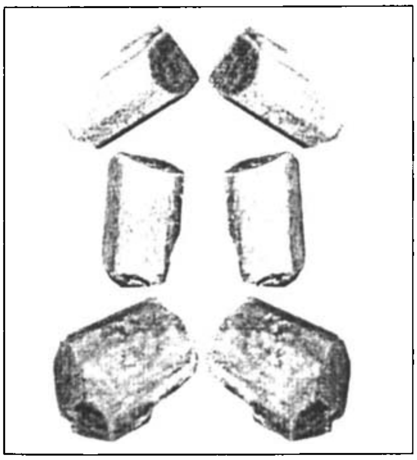

Figure 2. Views from different directions are required to decide whether the object is chiral or not.

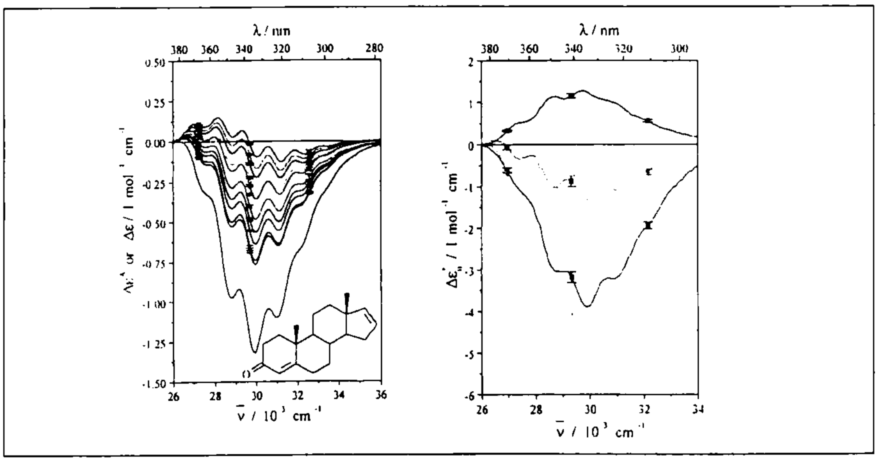

Figure 3. $\Delta\varepsilon$ (—) (T = 75°C) and temperature dependent $\Delta\varepsilon^A$ (from above T/°C = 31.2 to 64.0) (left) and the tensor components from the top (right) $\Delta\varepsilon^*_{33}$, $\Delta\varepsilon^*_{22}$, $\Delta\varepsilon^*_{11}$, and $\Delta\varepsilon^*_{11} + \Delta\varepsilon^*_{22}$ of androst-4,17-dien-3-one in the 'nematic state' of the liquid crystal phase ZLI-1695 (Merck).

phase, i.e. one of the 'supermolecules', from many directions in space. The mean value of a sufficient number of such measurements is equal to the result obtained from the ensemble of non-oriented 'anisotropic phases'. An experimental measurement based on the idea of the first definition is a CD measurement with a cholesteric phase built up by polydomains where the polydomains, the supermolecules, are isotropically distributed. Unfortunately, the stray light of the domains falsifies such a measurement severely and, therefore, such a measurement is highly questionable.

Is there a need for such an intricate definition of a chirality measurement with a chiral anisotropic phase? Is a measurement of CD with the anisotropic phase not sufficient to decide whether the system is chiral or not? The answer is no. For oriented achiral molecules of symmetry C_s, C_{2v}, D_{2d} or S_4, with suitable achiral biaxial long-range positional and/or orientational order the CD or ORD is different from zero because elements of the CD tensor $\Delta\varepsilon_{ij}$ are different from zero whereas the trace

$$\Delta\varepsilon = (\Delta\varepsilon_{11} + \Delta\varepsilon_{22} + \Delta\varepsilon_{33}) / 3 \qquad (2)$$

is equal to zero. This has been experimentally proven by optical rotation measurements on crystals with an achiral structure, i.e. without enantiomorphism [6].

There is one question left. Do chirality observations/measurements exist for an anisotropic phase? Two examples can be given: the CD can be measured with a light beam propagating along the optical axis of a chiral phase in a nematic state (ACD spectroscopy [7]) or in a chiral nematic state [8]. *Considering the chiral anisotropic phase as a supermolecule, as before, a chirality measurement for example with CD spectroscopy, is a CD measurement with the phase rotated about the direction of light propagation or a CD measurement with a phase which is rotationally symmetric about this direction* (figure 3). Without this rotational symmetry around the direction of light propagation, the results do not fulfill the requirements of a chirality measurement. A superposition of an achiral and a chiral effect, i.e. an elliptical effect, is obtained for which a decomposition into an achiral and a chiral part is either tedious or impossible.

Chirality function and chirality parameter

It is possible to describe the result of a chirality measurement as a function of phenomenological molecular parameters, so-called *chirality functions*. In the context of optical activity, Ruch and Schönhofer [9] have derived chirality functions from symmetry properties or permutation principles of ligands substituted on an achiral skeleton. Other chirality functions have been introduced by Kuz'min et al. [10] and Nordio [11] which have been applied to the chiral induction. In some cases pseudo-scalar parameters or pseudo-tensors have been introduced which correlate molecular quantities with the result of a chirality measurement. Examples are Lubensky's [12] or Dunmur and Osipov's [13] chirality parameters derived from pair interaction of two molecules or from expressions of the theory of optical activity. In the context of Monte Carlo simulations of chiral liquid crystal phases [14] the interaction potential can be decomposed into a sum of an achiral U_{ach} and a chiral, i.e. pseudo-scalar, energy U_{ch}. From this a chirality parameter c can be defined by

$$U = aU_{ach} + cU_{ch}. \qquad (3)$$

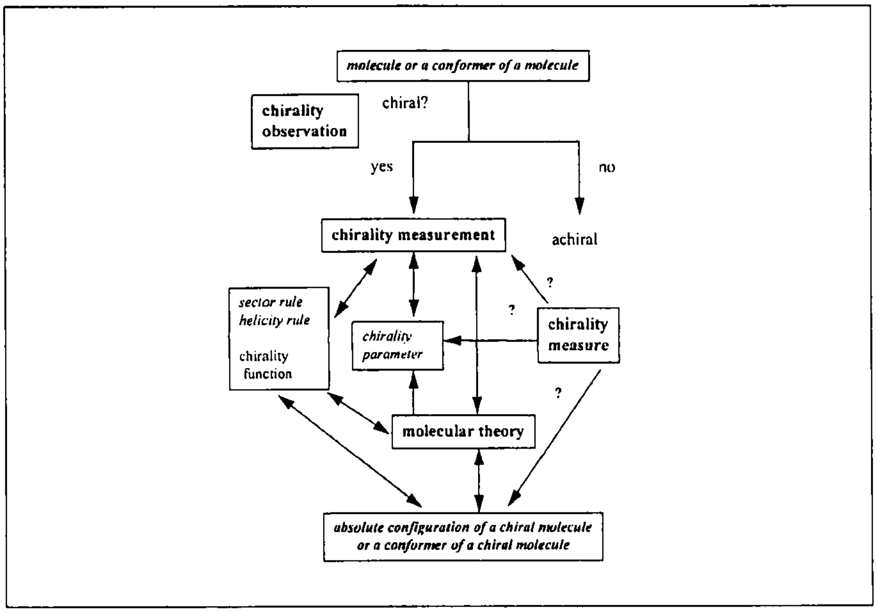

Figure 4. Correlation between the concepts chirality observation, chirality measurement, chirality function, chirality parameter, and chirality measure.

Chirality measure

In many fields of natural science a language has been introduced, for example with ferroelectricity or blue phases, where molecules have a 'small' or 'large' chirality. What does 'small or large chirality' mean? This notion correlates sign and size of special effects i.e. a large CD or a large helical twisting power (HTP) with the ability to produce blue phases. But neither CD nor HTP can be a measure for chirality because they do not fulfill the conditions for an appropriate chirality measure [15] which is: (1) it must differ from zero if the object is chiral (the quantity has no sign!), (2) it is invariant against similarity transformations, and (3) is a continuous function of one variable *C* (*C* ≡ degree of chirality).

The hierarchy of concepts

The concepts which have been discussed are summarized in the diagram given in figure 4 [4]. The arrows point out the direction in which the concepts can be correlated.

Enantiomers and their absolute configuration

The absolute determination of the absolute configuration can be performed with X-ray crystallographic analysis, where for compounds with chiral conformers, different configurations from the gaseous and fluid state are often obtained. The classical methods to determine a relative absolute configuration in the gaseous and fluid state are CD and/or ORD measurements (figure 1). To correlate the sign of the Cotton effect and the absolute configuration of the chromophore [16] either empirical sector or helicity rules have to be found, the exciton chirality method has to be applied or quantum mechanical calculations of the rotational strength have to be performed.

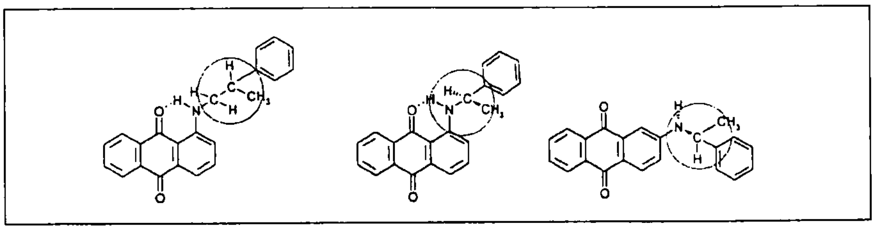

Figure 5. The asymmetric carbon atom as a chiral element and a chiral region (within the circle) within the concept of intramolecular chirality transfer [22].

Stabilization by chiral structures: chiral anisotropic and chiral isotropic phases

Not only chiral or racemic achiral compounds but also achiral compounds stabilize themselves by forming a chiral liquid, liquid crystalline or crystalline phase. Merocyanins with J aggregates in the fluid phase [17], dialkylsilylene polymers with a helical chain [18], racemic achiral atropisomers as binaphthyl [19], and also norganic systems such as $NaClO_3$ [20] with a cubic crystalline phase, can be given as examples. Thus experimentally one finds spontaneous separation into chiral phases constituted from atoms, ions, achiral molecules, molecules only with conformational chirality, and molecules with constitutional chirality from achiral or racemic achiral fluid states. Generally, the left and right handed systems are obtained in equal amounts, but often pure chiral forms or phases with an enantiomeric excess (ee) can be found. An accidentally faster initial nucleation of one form is often the starting point for the phase separation. In a phase with suprastructural chirality a diastereomeric interaction of the originally unstable chiral form of the molecule and the suprastuctural chirality of the phase forces the system into a preferred chiral phase.

Summarizing these experimental findings, it is not surprising that liquid crystal phases form one or two locally separated chiral phases spontaneously. There is an analogy to the crystallization of enantiomorphic crystals, but there may be a larger diversity of chiral structures [1] in liquid crystals because of their lower formation energies. The detailed mechanisms for the stabilization and the easy phase separation for liquid crystals in the two chiral forms are often unknown.

The intramolecular chirality transfer

Within the concept of Cahn *et al.* [21] for the classification of compounds, chiral elements like a chiral centre, i.e. an asymmetric carbon atom, a chiral axis or a chiral plane, have been introduced as the geometrical origin of chirality. Compounds with one and the same chiral element and with a different structure somewhat away from the chiral element, in the so-called 'achiral parts' of a molecule (figure 5)[3], can induce a chiral nematic phase with pitches of different size and sometimes also of different sign. Before discussing the transfer of the 'information chirality' between two adjacent levels of chirality, a concept of transferring chirality from a chiral element and its near surroundings—the chiral part of the molecule[3]—to the residue of the molecule—the 'achiral part'—has to be introduced. Accepting this concept of formal decomposition, one has to have always in mind that the molecular region taken as the 'chiral' and the 'achiral' part is only qualitatively defined. By interaction with the chiral region a distortion of the electronic structure or an excess of a chiral conformation can be induced in the 'achiral part' of the molecule. CD spectroscopy can serve as a tool to determine this transfer. For example the CD of a chromophore increases when the distance between the chromophore and the chiral centre decreases. For substituted aminoanthraquinones the transfer of the 'information chirality' from one and the same chiral ligand to the anthraquinone skeleton depends also on the position of substitution of the ligand or the number of carbon atoms between the asymmetric carbon atom of the ligand and the skeleton (figure 5, [22]).

Chirality transfer between the four levels of chirality

The question how chirality can be transferred from one level to an adjacent level and how the chirality of these levels is correlated is a logical consequence of the introduction of four levels of chirality. Especially for the mapping of chirality of a molecule (2nd level) onto the liquid crystal phase (3rd level) or vice versa—the intermolecular chirality transfer—these questions are of huge interest. But the question what does chirality transfer really mean has no simple answer. Chirality is not an extensive property. The question, how much chirality does a molecule possesses or how much chirality can be transferred to an adjacent level is not allowed in the sense of transportation of an amount of 'chirality' from one system to another. Chirality is information which can be transferred from one level to the other without being lost in the level from which it originated. Two statements are possible:

1 the information about the absolute configuration in one level is transferred to and stored by the absolute configuration of the adjacent level, and

2 the result of a chirality measurement of one level is correlated to the result of a chirality measurement of the chirality of the adjacent level.

For the discussion of the first point, a standard for the characterization of the absolute configuration of each level is needed. For molecules (2nd level) the Cahn–Ingold–Prelog nomenclature [21] *R* or *S* and *P* or *M* is available whereas, e.g. the helicity of a chiral nematic phase (3rd level) can only be given by *P* or *M*. If now a chiral dopant, the object, (the 2nd level) with a configuration *R*, e.g. induces a cholesteric phase of helicity *P*, then the information 'absolute configuration *R*' of the 2nd level is transferred to the helicity *P* of the 3rd level. If the chirality of a number of compounds and also their effect of mapping onto the phase are correlated, then a rule for the determination of the absolute configuration of an object is obtained:

2nd level	abs. config. of object 1	↔	abs. config. of object 2	↔	abs. config. of object 3	↔	....
	↕		↕		↕		↕
3rd level	abs. config. of the ind. phase 1	↔	abs. config. of the ind. phase 2	↔	abs. config. of the ind. phase 3	↔	....

For the second statement two cases can be discussed. The chirality measurements for the adjacent levels can be of the same or of different kind. The Cotton effect of the dopant (2nd level) can be compared to the Cotton effect of the induced chiral nematic phase (3rd level) which is, in general, larger by orders of magnitude. The sign of the Cotton effects of the molecule belonging to different absorption bands depends on the nature of the transition and the surroundings of the chromophore, the Cotton effects of the phase depend on the suprastructural chirality around the molecule and thus, can only be compared and correlated in special cases. Also in these situations it makes no sense to speak about an enhancement of chirality. There is an enhancement of the value of a chirality measurement in spite of the different origins of the effects. In cases like the chiral induction, the HTP, where no corresponding chirality measurement with the single molecules exists another kind of chirality measurement has to be taken instead. A chiral interaction potential from a 'chiral surface' may be a useful quantity [11] or, in a suitably chosen example even the CD or ACD of the compound [7, 22]. Also in these situations there is only an enhancement of a chirality measurement and not an enhancement of chirality.

Up to now, the chirality transfer from the level of molecules (2nd level) to the phase (3rd level) has been taken into consideration. An example of the transfer of chirality from the liquid crystal phase (3rd level) to the molecule (2nd level) is the liquid crystal induced CD (LCICD) [23].

Atoms ↔ Molecules

The chirality transfer from the level of atoms to the level of molecules can hardly be proven unless one argues with the homochirality of the animate world [24]. From an energetic point of view the transfer cannot

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[3] This nomenclature is not correct because the molecule is chiral as a whole. This expression is chosen because there is no better name for a molecular part where no chiral elements exist.

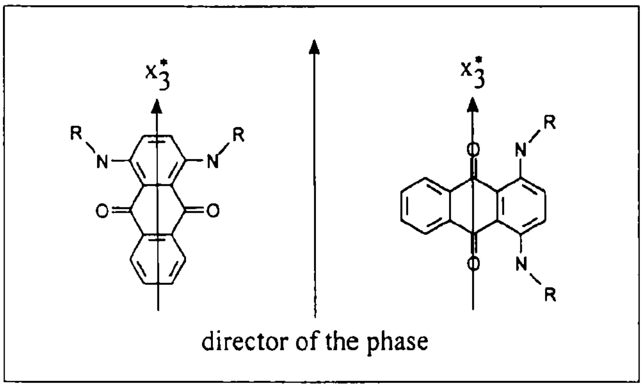


Figure 6. Switching, i.e. a rotation about 90°, of the orientation axis (x^*_3) by variation of *R*. The orientation axis is the principal axis of the order tensor to which the largest eigenvalue belongs or the axis with the best orientation in the phase [22].

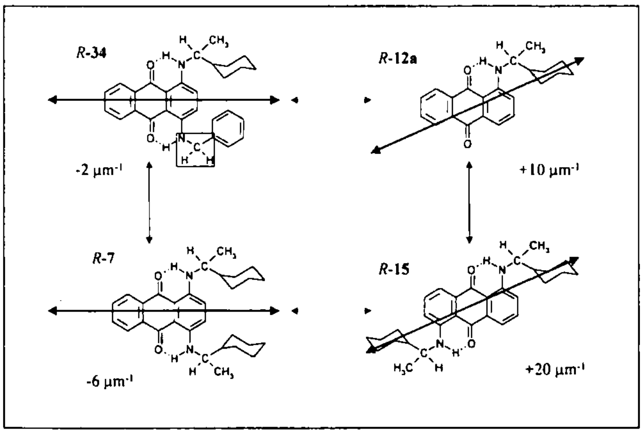


Figure 7. Additivity of the contributions of chiral centres introduced by substituted groups on a rigid molecular frame to the HTP and the influence of the rotation of the orientation axis (x_3) on the HTP.

be very large because of the very small diastereomeric interaction between atoms and chiral molecules. Probably, the homochirality is a consequence of this small diastereomeric energy and a number of subsequent processes which enhance the effect by further enrichment of one of the chiral forms. No influence of the weak interaction on chemical reactions performed in the laboratory can be detected with the experimental techniques currently available.

Molecule ↔ Phase: the intermolecular chirality transfer

A transfer of the 'information chirality' from the level of molecules onto a phase can be unequivocally proven. Chiral interactions change the structure of the phase, the planes, the lattice point or the orientation of a molecule in a lattice point (general position). This means that molecular chirality can be mapped onto an achiral phase and yields a suprastructural phase chirality (intermolecular chirality transfer). A simple example is given by the induction of a chiral nematic phase from a nematic phase; here the chirality of a molecule is transformed into the helicity of the phase. The size of the helical pitch is for dilute solutions, in general, proportional to the concentration of the chiral dopant. The achiral nematic phase acts as a molecular amplifier for measurable pseudo-scalar molecular properties by inducing measurable pseudo-scalar phase properties which are, in general, larger in size.

There are two important experimental findings with the intermolecular chirality transfer. At first, there is the additivity of group contributions to the helical twisting power (HTP, equation (4)) of a compound possessing different chiral centres which are far away from each other [22]. Secondly, the intermolecular chirality transfer depends on the orientation of the principal axes of the order tensor with respect to the molecular frame of the chiral molecule and also on the orientation of the chiral groups with respect to the principal axes of the order tensor [22]. The effect of the rotation of the orientation axis by variation of the substitution pattern or by varying *R* (figure 6) within a series of aminoanthraquinones is presented in figure 7. The bold solid arrows represent the orientation axes of the molecules. Rotating the orientation axis by substitution with the same chiral ligand in the 1,4- and in 1,5-positions results in a variation of size and sign of the HTP (figure 7).

As discussed in connection with the CD spectra of oriented molecules (ACD spectroscopy), the phase 'sees' the molecule from different directions. Such behaviour is typical for tensorial properties like the CD tensor for ACD spectroscopy [7]. Introducing a chirality interaction tensor W_{ij} for guest-host systems, which is given by a contraction of a chirality tensor C_{ij} of the molecule and a phase tensor L_{ij}, i.e. $W_{ij} = \sum_{lk} L_{ik}C_{kj}$, equations (4) and (5) can be obtained for the HTP [25], where the effect is analogous to the ACD given by a sum of products of the chirality interaction tensor and the order tensor:

$$\mathrm{HTP} = \left\{g^*_{1133}\, W^*_{11} + g^*_{2233} W^*_{22} + g^*_{3333} W^*_{33}\right\}, \tag{4}$$

$$\mathrm{HTP} = \left\{\tfrac{1}{3}W + \left(W^*_{33} - \tfrac{1}{3}W\right)S^* + \left(W^*_{22} - W^*_{11}\right)D^*\sqrt{3}\right\}\cdot \tag{5}$$

g_{ijkl} are the orientational distribution coefficients (equation (6)) for a guest and the HTP = $p^{-1}\,x^{-1}$, where x is the mole fraction. The orientational distribution function $f(\Omega)$ with $\Omega \equiv (\alpha\beta\gamma)$ defines the g_{ijkl} by

$$g_{ijk} = \frac{1}{8\pi^2}\int f(\Omega)a_{ik}(\Omega)a_{jl}(\Omega)\,d\Omega, \tag{6}$$

where the $a_{ij}(\Omega)$ are elements of the transformation matrix from the space fixed to the molecule fixed coordinate system. The order parameters are then given by

$$S^* = \tfrac{1}{2}\left(3g^*_{3333} - 1\right) \quad \text{and} \quad D^* = \left(\sqrt{3}/2\right)\left(g^*_{2233} - g^*_{1133}\right)\cdot \tag{7}$$

With knowledge of the order tensor and the temperature dependence of the HTP, the diagonal elements of the chirality interaction tensor W^*_{ii} with respect to the principal axes of the order tensor can be evaluated.

The presentation of the HTP as sum of products (equations (4) and (5)) allows an easy explanation for one of the four mechanisms known for the helix inversion. In case of the dependence of the HTP on the orientation of the orientation axis [22], the terms $g^*_{ii33}W^*_{ii}$ as a function of S^* contribute to the HTP with a different size and even sign if the coordinates W^*_{ii} are of different sign. For the binaphthol Dioxepin a sign inversion takes place for large S^* values because the contribution belonging to the orientation axis $g^*_{3333}W^*_{33}$ is positive and the tensor coordinate W^*_{22} is negative.

Phase ↔ Form or the shape of the macroscopic object

Whether there is a provable transfer from the phase chirality to the chirality of the external structure is a problem which has not been discussed extensively as yet. Chiral molecules can crystallize with a chiral macroscopic crystalline form, i.e. in space group like $\bar{4}\,2m$, $\bar{4}$ etc. but also often with an inversion centre, i.e. in a crystal of an achiral form [26].

References

1 Shirota, K., Yaginuma, M., Sakai, T., Ishikawa, K., Takezoe, H., and Fukuda, A., 1996, *Jpn. J. appl. Phys.*, **35**, 2275.
Heppke, G., and Moro, D., 1998, *Science*, **279**, 1872.

2 Thomson, W., 1904, *The Robert Boyle Lecture*, Oxford University Junior Scientific Club, May 16, 1893, in Baltimore Lectures (London: C. J. Clay & Sons).

3 Zabrodski, H., and Avnir, D., 1995, *J. Am. chem. Soc.*, **117,** 462.

4 Kuball, H.-G., Memmer, R., and Türk, O., 1999, *Ferroelectrics*, edited by S. Lagerwall and L. Komitov, in press (World Scientific Press).

5 Ruch, E., and Schönhofer, A., 1970, *Theor. Chim. Acta*, **19,** 225.

6 Hobden, M. V., 1967, *Nature*, **216,** 678.

7 Kuball, H.-G., and A. Schönhofer, 1994, *Circular Dichroism Principles and Applications*, edited by K. Nakanishi, N. Berova and R. W. Woody (New York: VCH Publishers Inc.), p. 85.

8 Saeva, F. D., 1979, *Liquid Crystals*, edited by F. D. Saeva (New York, Basel: Marcel Dekker, Inc.), p. 249.

9 Ruch, E and Schönhofer, A., 1970, *Theor. Chim. Acta*,**19,** 225.

10 Kutulya, L. A., Kuz'min, V. E., Stel'makh, I. B., Handrimailova, T. V., and Shtifanyuk, P. P., 1992, *J. Phys. Org. Chem.*, **5,** 308.

11 Ferrarini, A., and Nordio, P. L., 1998, *J. chem. Soc.*, Perkin Trans., **2,** 455.

12 Lubensky, T. C., Harris, A. B., Kamien, R. D., and Gu Yan, 1998, *Ferroelectrics*, **212,** 1.

13 Osipov, M. A., Pickup, B. T., and Dunmur, D. A., 1995, *Mol. Phys.*, **84,** 1193.

14 Bates, M. A., Luckhurst, G. R., 1999, *Struct.Bond.*, **94,** *65.*

15 Buda, A. B., Auf der Heyde, Th., and Mislow, K., 1992, Angew. Chem., 104, 1012.

16 *Circular Dichroism Principles and Applications*, 1994, edited by K. Nakanishi, N. Berova and R. W. Woody (New York: VCH Publishers Inc.).

17 De Rossi, U., Dähne, S., Meskers, S. C. J., and Dekkers, H. P. J. M., 1996, *Angew. Chem.*, **108,** 827.

18 Frey, H., Möller, M., Turetskii, A., Zotz, B., and Matysaszenski, K., 1995, *Macromolecules*, **28,** 5498.

19 Wilson, K. R., and Pincock, R. E., 1975, J. *Am. chem. Soc.*, **97,** 1474; Kress, R. B., Duesler, E. N., Etter, M. C., Paul, I. C., and Curtin, D. Y., 1980, J. *Am. chem. Soc.*, **102,** 7709.

20 McBride, J. M., and Carter, R. L., 1991, *Angew. Chem.*, **103,** 298; Kondepudi, D. K., Kaufmann, R. J., and Singh, N., 1990, *Science*, **250,** 975.

21 Cahn, R. S., Ingold, C., and Prelog, V., 1966, *Angew. Chem. Intern. Edit.*, **5,** 386.

22 Kuball, H.-G., Brüning, H., Müller, Th., Türk, O., and Schönhofer, A., 1995, *J. mater. Chem.*, **5,** 2167; Kuball, H.-G., and Brüning, H., 1998, *Chirality*, **9,** 407.

23 Guo, J.-X, and Gray, D. G., 1995, *Liq. Cryst.*, **18,** 571.

24 Janoschek, R., 1991, *Chirality-From Weak Bosons to the ∝-Helix*, edited by R. Janoschek (Berlin, Heidelberg: Springer Verlag), p. **18.**

25 Kuball, H.-G., Türk, O., Kiesewalter, I., and Dorr, E., 1999, in preparation.

26 Kitaigorosdsky, A. I., 1973, *Molecular Crystals and Molecules* (New York, London: Academic Press).

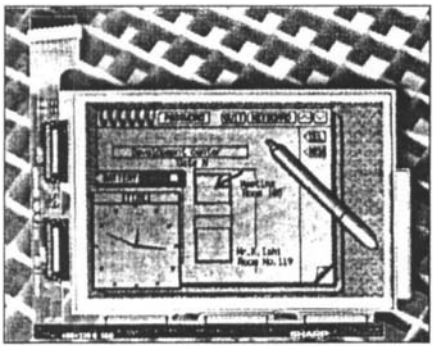
COMPANY NEWS

Merck moves to Southampton

Merck KGaA, the German speciality chemical company, has moved its UK R & D facility from Poole, Dorset, to Southampton University's Highfield Campus, while it constructs a purpose-built laboratory on the University's Chilworth Science Park. The new laboratory will provide facilities for up to 30 research staff working on new functional materials, including liquid crystals, advanced inorganic materials and superconductors.

Sharp celebrates 25 years of liquid crystal technology

Twenty five years ago Sharp manufactured the world's first pocket calculator with a liquid crystal display, and triggered a wave of innovation, the end of which is not yet in sight. Liquid crystal displays have become a key technology, and are used in a wide range of instruments and devices. 'The liquid crystal display has become a universal user interface, without which the use of complex digital functions would be impossible', said Martin Beckmann, press spokesman for Sharp Electronics (Europe). 'For this reason Sharp are focusing a large part of our world-wide research on the further development of this technology'. Recently (see *Liquid Crystals Today*, **8**, No. 4) Sharp produced an extremely light and robust plastic liquid crystal module (see figure).



The new extremely light but also very robust plastic LC modules do not need a costly frame especially in the case of much used equipment like cell phones and pagers.

Sharp researchers are working hard in a bid to realise their vision of a paper-thin computer, using a new technology which will allow the integration of switching circuits in a wafer-thin layer on the glass of a liquid crystal display. The vision is of a foldable computer: a type of electronic paper for the next century. Speaking with 25 years of experience of liquid crystal technology, Atsushi Asada, management consultant with Sharp, said: 'You should never lower your technological expectations'.

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CRL to manage new European display project

CRL, a Scipher company based in Hayes, London, UK, is to manage a new European display project: HELICOS (Hand-held Reflective Colour Displays). The 4 MECU project will run over 2 years, and involves major players from the European display industry, including ASULAB, Thomson LCD, IMEC, ALCATEL, the University of Stuttgart and Tecdis. The main objectives of the project are to develop and demonstrate passive matrix and active matrix reflective liquid crystal displays for use in portable IT products such as palmtop computers and emerging computer/telecommunications products. The main developments will take place in the optimization of liquid crystal display technologies. Approaches based on the use of dichroic dyes, light scattering effects and stabilized cholesteric textures, none of which require the use of polarizers, will be investigated.

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