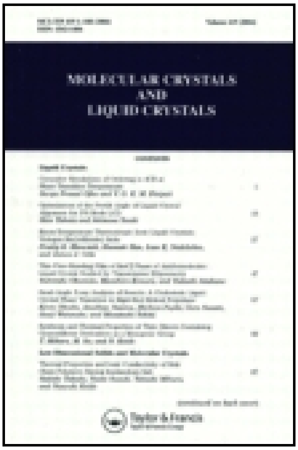

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Transformation Properties of Order Parameters for a Nematic Liquid Crystal Phase

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To cite this article: Hans-Georg Kuball, Hans-Dieter Schwaben, Volker Dolle & Alfred Schönhofer (1987): Transformation Properties of Order Parameters for a Nematic Liquid Crystal Phase, Molecular Crystals and Liquid Crystals, 144:5, 337-344

To link to this article: http://dx.doi.org/10.1080/15421408708084227

Mol. Cryst. Liq. Cryst., 1987, Vol. 144, pp. 337–344

Printed in the United States of America

Transformation Properties of Order Parameters for a Nematic Liquid Crystal Phase

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(*Received August 8, 1986*)

The two order parameters ρ, η, defined by Saupe for a nematic liquid crystal phase, are rewritten as linear combinations of orientational distribution coefficients g^0_{ijkl} which transform as second rank tensor coordinates with regard to the first and second pairs of indices. The motion of a point (ρ, η) within the order triangle, defined by this description, under transformations of the molecule fixed coordinate system is analyzed. For the determination of order parameters by spectroscopic methods two coordinate systems are of particular interest which do not coincide for molecules of symmetry C_1, C_2, C_i, C_s or C_{2h}: the principal axes of g^0_{ij33} and of the spectroscopic tensor, respectively. Most order parameters given in literature refer to the latter system in spite of the fact that such quantities cannot be compared to each other for different molecules or methods of measurements. For steroid nitrites, as an example, it is shown that $\eta^* \neq 0$.

Keywords: nematic phase, order parameters, tensorial properties

Orientational order of anisotropic systems, e.g. nematic liquid crystals, can be characterized by an orientational distribution function $f = f(\alpha, \beta, \gamma)$ where α, β and γ are the Eulerian angles. From this function a set of orientational distribution coefficients

$$g_{ij\ldots kl\ldots} = \frac{1}{N} \iiint f(\alpha, \beta, \gamma)\, a_{ik}\, a_{jl\ldots} \sin\beta \, d\alpha d\beta d\gamma \qquad (1)$$

can be derived which may be classified with respect to their tensor properties. N is a normalization constant; a_{ij} are the elements of an orthogonal transformation matrix from the space fixed (x'_i) to the molecule fixed (x_i) orthogonal Cartesian coordinate system.

For an absorption process (IR, UV), the measurable quantity $Y_1 = \epsilon_1$ (often named also $\epsilon_{\|}$) is related to the transition moment tensor $X_{ij} = \epsilon_{ij}$ by the equation[1]

$$Y_1 = g_{ij33} X_{ij}. \tag{2}$$

For circular dichroism (CD), the same equation holds if the quantity $Y_1 = \Delta\epsilon^A$ (ACD) is measured with a light beam propagating parallel to the optical axis of a uniaxial system ($\| x'_3$; $f = f^0(\beta, \gamma)$). Here $X_{ij} = \Delta\epsilon_{ij}$ represents the tensor of rotation.

The orientational distribution coefficients g_{ijkl} transform as tensor coordinates of second rank with regard to the first and second pair of indices if the molecule fixed and the space fixed coordinate systems are changed, respectively. For uniaxial systems with optical axis in x'_3 direction, there are only five independent parameters g^0_{ij33}. Three of them describe the choice of the molecule fixed coordinate system, e.g. relative to the principal axes x^*_i of the symmetric tensor g^0_{ij33}. The remaining two orientational distribution coefficients are a measure of the order of the distribution and can be transformed into the two order parameters ρ, η introduced by Saupe:

$$\rho = \frac{1}{2}(3\, g^0_{3333} - 1), \tag{3a}$$

$$\eta = \frac{1}{2}(2\, g^0_{2233} + g^0_{3333} - 1). \tag{3b}$$

With these two parameters, an order triangle can be defined in the ρ, η-plane (Figure 1). The hatched region is sufficient to describe the order in a uniaxial system if the convention $g^0_{3333} \geqslant g^0_{2233} \geqslant g^0_{1133}$ is accepted, i.e. every possible function $f = f^0(\beta,\gamma)$ has an image point in this region.[2] Of course, different functions having the same $g^0_{\underline{ii}33}$† are mapped into the same point.

The points of the triangle Figure 1 can also be interpreted in a different way. For a given uniaxial distribution, differently chosen molecule fixed

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†Underlined indices are not to follow the summation convention.

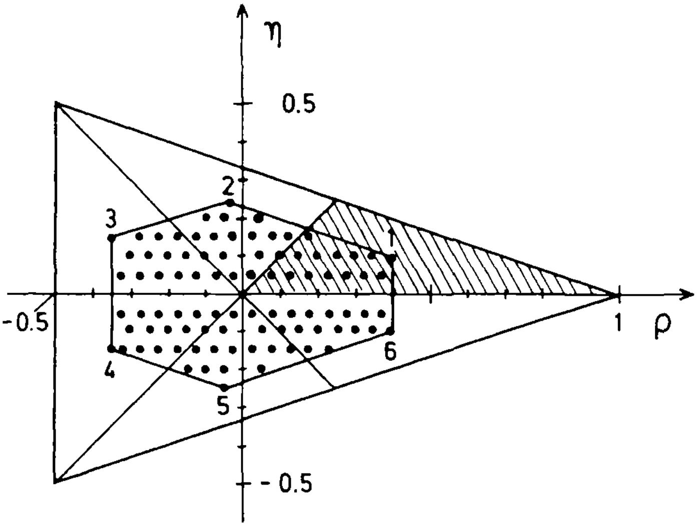


FIGURE 1 Order triangle

$$(\rho_1 = \rho_6 = \rho^*, \eta_1 = -\eta_6 = \eta^*; \rho_2 = \rho_5 = -\frac{1}{2}(\rho^* - 3\eta^*),$$
$$\eta_2 = -\eta_5 = \frac{1}{2}(\rho^* + \eta^*); \rho_3 = \rho_4 = -\frac{1}{2}(\rho^* + 3\eta^*), \ \eta_3 = -\eta_4 = \frac{1}{2}(\rho^* - \eta^*))$$

coordinate systems yield, in general, different image points; a change of the x_i system results in a motion of the point (ρ, η) in the triangle. Three special coordinate systems, essential for the discussion of order parameters in literature, will be presented in more detail in the following (Table I). The first column applies to an arbitrarily chosen molecule fixed coordinate system. The quantities in the second and third column refer to the principal axes of the orientational distribution coefficients g^0_{ij33} and of the molecular property X_{ij}, respectively. For molecules of symmetry C_1, C_2, C_i, C_s or C_{2h} these axes, in general, will not coincide; for all other symmetries they do. In the first case,

TABLE I

Notation of order parameters	ρ, η	ρ^*, η^*	ρ^+, η^+	$\hat{\rho}, \hat{\eta}$
Coordinate system	x_i	x^*_i	x^+_i	$\hat{x}_i$
Diagonal tensors	—	g^*_{ij33}	X^+_{ij}	—
Non-diagonal tensors	X_{ij}, g^0_{ij33}	X^*_{ij}	g^+_{ij33}	$\hat{X}_{ij}, \hat{g}_{ij33}$
Special conditions and conventions	—	$g^*_{3333} \geqslant g^*_{2233} \geqslant g^*_{1133}$	—	$\hat{g}_{ij33} \hat{X}_{ij} = \hat{g}_{3333} \hat{X}_{kk}$

therefore, the x_3^* and x_3^+ axes will be different, and so will be the points (ρ^*, η^*) and (ρ^+, η^+). Starting from the point (ρ^*, η^*), every point in the dotted hexagon of Figure 1 can be reached by a suitable transformation of the molecule fixed coordinate system. For $\eta^* = 0$, the dotted area becomes a triangle.

The order parameters ρ^*, η^* are solely determined by the type and magnitude of the orientational order while ρ^+, η^+ in addition to this—by choice of the molecule fixed coordinate system—also include properties of X_{ij}. Therefore, ρ^+, η^+ are not very suitable quantities when comparing order parameters of different molecules. This is a problem for molecules of low symmetry which has often been overlooked in literature where most of the order parameters determined refer to x_i^+. Furthermore, for one and the same system different methods of measurement can lead to different ρ^+, η^+ depending on the properties of the respective X_{ij}.

A large number of order parameters given in literature are calculated assuming that x_i^* and x_i^+ coincide and that, furthermore, there is only one transition moment i.e. $X_{11}^+ = X_{22}^+ = 0$. In most cases this approximation seems to work very well. According to the equation

$$\frac{Y_1 - Y_{\text{iso}}}{2Y_{\text{iso}}} = \frac{1}{2}(3\,q_{33}^* - 1)\,\rho^* + \frac{3}{2}(q_{22}^* - q_{11}^*)\,\eta^*,$$
$$Y_{\text{iso}} = \frac{1}{3}X_{kk}^+ = \epsilon_{\text{iso}},\,\Delta\epsilon_{\text{iso}};\qquad q_{ii}^* = \frac{X_{ii}^*}{X_{kk}^+}, \tag{4}$$

resulting from Eqs. (2) and (3), it amounts to

$$\frac{Y_1 - Y_{\text{iso}}}{2Y_{\text{iso}}} = \rho^* = \rho^+. \tag{5}$$

If the presuppositions are not fulfilled eq. (5), of course, is not correct. But there may exist another special coordinate system $\hat{x}_i$ in which the order parameter $\hat{\rho}$ equals the measurable quantity,

$$\frac{Y_1 - Y_{\text{iso}}}{2\,Y_{\text{iso}}} = \hat{\rho}, \tag{6}$$

thus pretending the situation to Eq. 5. This can be seen from the transformation properties of ρ, η. The order parameters referring to an arbitrary molecule fixed coordinate systems are related to ρ^*, η^* by

$$\begin{aligned}\rho &= \frac{1}{2}(3\,a_{33}^2 - 1)\,\rho^* + \frac{3}{2}(a_{32}^2 - a_{31}^2)\,\eta^*,\\ \eta &= \frac{1}{2}(a_{23}^2 - a_{13}^2)\,\rho^* + \frac{1}{2}(a_{11}^2 + a_{22}^2 - a_{12}^2 - a_{21}^2)\,\eta^*,\end{aligned} \tag{7a}$$

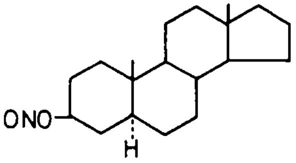
where $x_i = a_{ij}(\alpha_0, \beta_0, \gamma_0)\,x_j^*$.

For an $\hat{x}_i$ system to exist there must be, by comparison of Eqs. (4) and (7a)

$$0 \leqslant a_{3i}^2 = q_{ii}^* \leqslant 1, \tag{8}$$

i.e. all X_{ii}^* must be of the same sign. This applies for IR and UV and sometimes also for ACD. As the a_{3i} only depend on α_0, β_0 the angle γ_0 of the transformation remain arbitrary. By means of Eqs. (2) and (3) the condition (6) can also be written as

$$\hat{g}_{ij33}\,\hat{X}_{ij} = \hat{g}_{3333}\,\hat{X}_{kk}. \tag{9}$$



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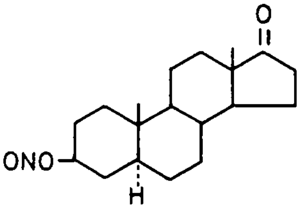

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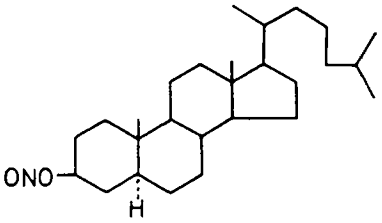

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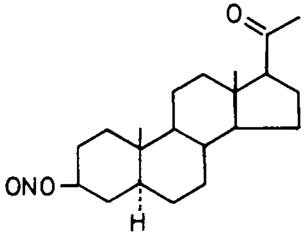

4

FIGURE 2 Steroid nitrites 1 to 4

Unfortunately, the orientation of the $\hat{x}_i$ system depends strongly on the molecular property X_{ij} which in many cases is not known very well. Therefore, a discussion of $\hat{\rho}$ as a function of molecular structure parameters is not without problems.

These considerations show also the difficulty to prove $\eta^* \neq 0$ for molecules of low symmetry. In the preceding papers a special procedure has been given for such a proof. For the steroid nitrites, Figure 2, another procedure will be discussed in the following. For $\underline{1}$ to $\underline{4}$ the UV and ACD spectra (ϵ_{iso}, $\Delta\epsilon_{iso}$, $\Delta\epsilon^A$) are given in Figures 3 and 4 besides the degree of polarization $P = (\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$ [ϵ_2 often named also $\epsilon\perp$]. ϵ_{iso} and $\Delta\epsilon_{iso}$ are equal for all compounds. From this we assume that ϵ_{ij} and $\Delta\epsilon_{ij}$ are equal, too. This is plausible from the

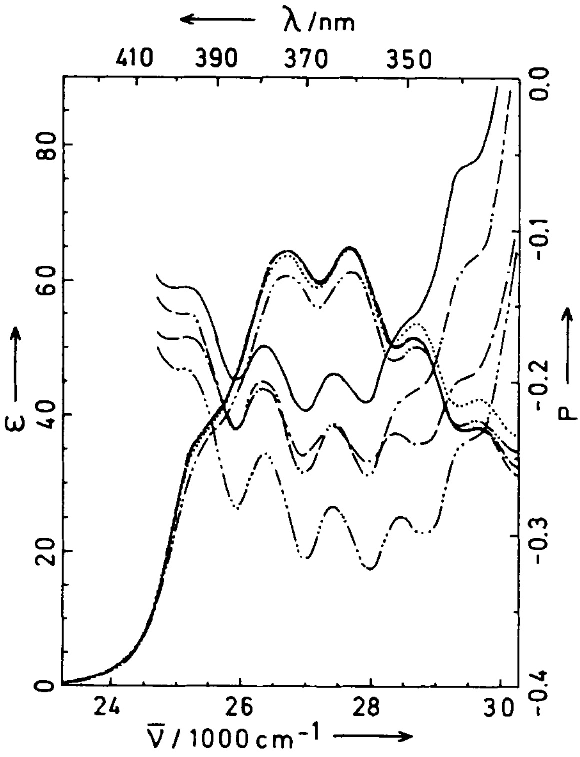

FIGURE 3 UV absorption (T = 353.2 K) and degree of polarization (T = 310.7 K) in cholesteryl chloride/cholesteryl laurate (CC/CL), 1.8:1 by weight) of
$\underline{1}$ (• • • ϵ_{iso}, — P), $\underline{2}$ (– – – ϵ_{iso}, – • • • P),
$\underline{3}$ (– • – ϵ_{iso}, – –• P), $\underline{4}$(– • • ϵ_{iso}, – – • • P).

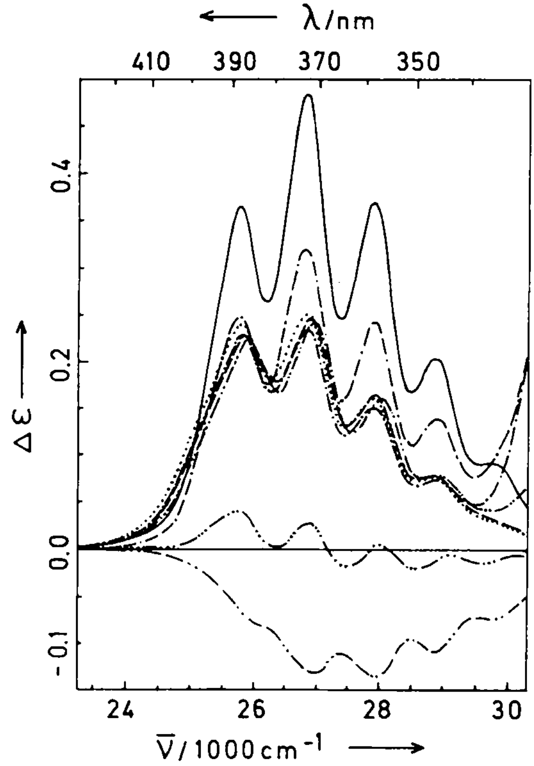

FIGURE 4 CD (T = 353.2 K) and ACD (T = 310.7 K) spectra in CC/CL (1.8:1 by weight) of
$\underline{1}$ (• • • $\Delta\epsilon_{iso}$, — $\Delta\epsilon^A$), $\underline{2}$ (– – – $\Delta\epsilon_{iso}$, –• • • $\Delta\epsilon^A$),
$\underline{3}$ (–•– ϵ_{iso}, – –•$\Delta\epsilon^A$), $\underline{4}$ (–• • $\Delta\epsilon_{iso}$, – –•• $\Delta\epsilon^A$).

spectroscopic point of view because the chromophore —ONO† is far away from those parts of the molecules where they are different. As can be seen from Figures 3 and 4, the following inequalities hold:

$$(\epsilon_1 - \epsilon_{iso})_{\underline{3}} < (\epsilon_1 - \epsilon_{iso})_{\underline{4}} \simeq (\epsilon_1 - \epsilon_{iso})_{\underline{2}} < (\epsilon_1 - \epsilon_{iso})_{\underline{1}} \qquad (10)$$

$$(\Delta\epsilon_1^A - \Delta\epsilon_{iso})_{\underline{4}} < (\Delta\epsilon^A - \Delta\epsilon_{iso})_{\underline{3}} < (\Delta\epsilon^A - \Delta\epsilon_{iso})_{\underline{2}}$$

$$< (\Delta\epsilon^A - \Delta\epsilon_{iso})_{\underline{1}}, \qquad (11)$$

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†The —ONO group leads to conformers. Because the concentration ratios of these conformers are not expected to vary from $\underline{1}$ to $\underline{4}$, this is without any consequence for the argumentation given here.

$$(\Delta\epsilon^A - \Delta\epsilon_{\mathrm{iso}})_i > 0 \qquad i = \underline{1}, \underline{2}, \tag{12}$$

$$(\Delta\epsilon^A - \Delta\epsilon_{\mathrm{iso}})_i < 0 \qquad i = \underline{3}, \underline{4}, \tag{13}$$

If $\eta^* = 0$, $Y_1 - Y_{\mathrm{iso}}$ is proportional to ρ and, therefore, the sequence of the compounds should be the same in the inequalities (10) and (11). Different sequences demand $\eta^* \neq 0$. Furthermore, from inequalities (10) to (13) a sequence of $(\eta^*/\rho^*)_i$ can be derived, using Eq. (4):

$$\left(\frac{\eta^*}{\rho^*}\right)_{\underline{4}} < \left(\frac{\eta^*}{\rho^*}\right)_{\underline{3}} < \left(\frac{\eta^*}{\rho^*}\right)_{\underline{2}} < \left(\frac{\eta^*}{\rho^*}\right)_{\underline{1}}. \tag{14}$$

In a rough way of speaking, this sequence can be understood by the width/length ratio similarly to the behaviour of the ketosteroids.[4]

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