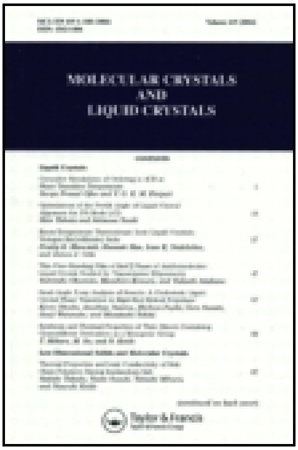


Molecular Crystals and Liquid Crystals

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

Order Parameters of Guest-Host Systems

J. Altschuh [a] , R. Weiland [a] , J. V. Kosack [a] , H. Schulze [a] , A. Strauss [a] , M. Kappus [a] , P. Kau [a] & H.-G. Kuball [a]

[a] Fachbereich Chemie der Universität Kaiserslautern, D-6750, Kaiserslautern, Germany

To cite this article: J. Altschuh , R. Weiland , J. V. Kosack , H. Schulze , A. Strauss , M. Kappus , P. Kau & H.-G. Kuball (1984): Order Parameters of Guest-Host Systems, Molecular Crystals and Liquid Crystals, 113:1, 321-327

To link to this article: http://dx.doi.org/10.1080/00268948408071692

Mol. Cryst. Liq. Cryst., 1984, Vol. 113, pp. 321-327
0026-8941/84/1134-0321/$15.00/0

Printed in the United States of America

ORDER PARAMETERS OF GUEST-HOST SYSTEMS

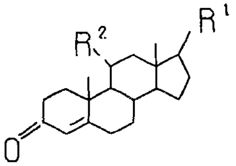
J. ALTSCHUH, R. WEILAND, J.V. KOSACK, H. SCHULZE,
A. STRAUSS, M. KAPPUS, P. KAU, and H.-G. KUBALL
Fachbereich Chemie der Universität Kaiserslautern,
D-6750 Kaiserslautern, Germany

Abstract For a guest-host system the relative order parameters of the guest and the host are determined for one and the same sample from the circular dichroism or the UV absorption spectra and the optical rotatory dispersion, respectively. While the host is a compensated nematic phase (cholesteryl chloride/cholesteryl laurate), several optically active 4-en-3-one steroids serve as guests. It has been shown that the order of the host varies with different guests and that sequences of increasing order for the guest and for the host in presence of the distinct guests do not coincide.

INTRODUCTION

Guest-host systems have a strong bearing on the application in the field of liquid crystal displays[1]. In this context investigations on the order parameters are of central interest. Whereas the determination of the order parameter of the guest molecule -usually a dye- is extensively described in literature[2], knowledge on the host order parameter or on guest and host is found only rarely[3].

In this paper we describe the determination of order parameters of the guest and the host relative to a standard (relative order parameters) for one and the same solution[4]. The host used is a compensated nematic phase consisting of cholesteryl chloride and cholesteryl laurate (CC/CL; 1.8:1 by weight) oriented by a dc electric field ($2\cdot10^6$ V/m). A number of optically active 4-en-3-one steroids differently substituted in the 11α- and 17β-position serve as guests (fig. 1). The order parameters of the guest are evaluated



	R^1	R^2
1	$-OH$	$-H$
2	$-O\overset{\overset{O}{\|}}{C}CH_3$	$-H$
3	$-O\overset{\overset{O}{\|}}{C}CH_2CH_3$	$-H$
4	$-O\overset{\overset{O}{\|}}{C}CH_2CH_2C_5H_9$	$-H$
5	$-O\overset{\overset{O}{\|}}{C}(CH_2)_5CH_3$	$-H$
6	$-O\overset{\overset{O}{\|}}{C}C_6H_5$	$-H$
7	$-\overset{\overset{O}{\|}}{C}CH_3$	$-H$
8	$-CH(OH)CH_3$	$-H$
9		$-H$
10	$-\overset{\overset{O}{\|}}{C}CH_3$	$-O\overset{\overset{O}{\|}}{C}CH_2CH_3$
11	$-\overset{\overset{O}{\|}}{C}CH_3$	$-O\overset{\overset{O}{\|}}{C}(CH_2)_5CH_3$

FIGURE 1. The guest molecules

from the UV absorption or circular dichroism (ACD) spectra in the spectral region of the $n-\pi^*$ transition of the enone chromophore. From the intrinsic optical rotatory dispersion (AORD) of the matrix molecules CC and CL the order parameters of the host can be calculated[5].

THEORETICAL BACKGROUND AND RESULTS

From measurements of the ACD ($\Delta\varepsilon^A$), AORD ($[M^A]$) or UV spectra (ε_β)+) of an anisotropic sample the calculation of orientational distribution coefficients g^o_{ijkl} or the order parameters ρ and η is possible according to eq. (1) to (3)[4-6] if the molecular quantity X_{ij} is known.

$$Y_{\beta\beta} = Y_\beta = g^o_{ij\beta\beta}X_{ij} \quad (\beta=1,2;\ \text{no summation}) \tag{1}$$ ++)

$$Y_\beta \equiv \Delta\varepsilon^A,\quad [M^A]\ ,\ \varepsilon_1,\ \varepsilon_2$$

$$g^o_{ijkl} = \frac{1}{4\pi}\int f(\beta,\gamma)a_{ik}a_{jl}\,\sin\beta d\beta d\gamma \tag{2}$$

$$\rho = (3g^o_{3333} - 1)/2 \tag{3a}$$

$$\eta = (2g^o_{2233} + g^o_{1133} - 1)/2 \tag{3b}$$

$X_{ij} \equiv \Delta\varepsilon_{ij}$, M_{ij} and ε_{ij} are the tensors of the CD, ORD and the UV absorption, respectively, $f(\beta,\gamma)$ is the orientational distribution function for a uniaxial system, where the optical axis is chosen parallel to the space-fixed x_3'-axis. a_{ij} are the elements of the transformation matrix from the space- (x_i') to the molecule-fixed (x_i) coordinate system and β, γ

+) For $\Delta\varepsilon^A$ and $[M^A]$the polarized light beam propagates parallel to the optical axis while for ε_1 and ε_2 the light beam is polarized parallel and perpendicular to the optical axis, respectively.

++) We use the index notation for vectors and tensors.

are Eulerian angles.

For the analysed $n-\pi^*$ transition of the molecules studied the tensor X_{ij} is not available in a satisfactory way. We therefore confine ourselves to the calculation of relative order parameters defined by eqs. (4) to (6) using $\underline{3}$ as the reference. For the guest follows

$$r_G(\underline{i},ACD) = \frac{(\Delta\varepsilon^A - \Delta\varepsilon_{iso})_{\underline{i}}}{(\Delta\varepsilon^A - \Delta\varepsilon_{iso})_{\underline{3}}}\ , \tag{4}$$

$$r_G(\underline{i},UV) = \frac{(\varepsilon_{iso} \cdot R)_{\underline{i}}}{(\varepsilon_{iso} \cdot R)_{\underline{3}}}\ , \tag{5}$$

and for the host in the presence of guest $\underline{i}$ results

$$r_H(\underline{i}) = \frac{([M^A] - [M_{iso}])_{\underline{i}}}{([M^A] - [M_{iso}])_{\underline{3}}}\ . \tag{6}$$

$\Delta\varepsilon_{iso}$, $[M_{iso}]$, and ε_{iso} are the CD, ORD, and absorption of the isotropic solution (T=80 ^oC), respectively. R is the degree of anisotropy. The results for r_G, r_H and r_G/r_H which are mean values from measurements at different wavelengths are shown in fig. 2. $r_G(\underline{i},ACD)$ and $r_G(\underline{i},UV)$ agree within the experimental error and therefore the mean value is used. $r_G(\underline{i})/r_H(\underline{i})$ is a scale for the guest order with respect to a constant order of the matrix.

From eqs. (1) and (3) results:

$$r = \frac{(\rho + Q\eta)_{\underline{i}}}{(\rho + Q\eta)_{\underline{3}}}\ , \tag{7}$$

$$Q = \frac{3(X_{22} - X_{11})}{2X_{33} - X_{11} - X_{22}}\ . \tag{8}$$

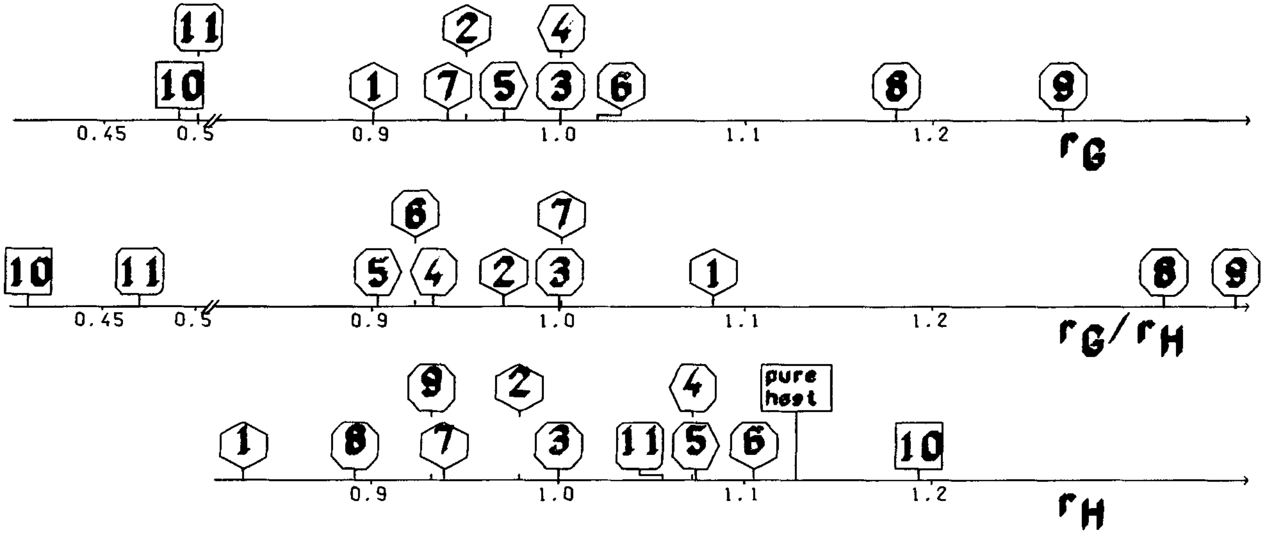


FIGURE 2. The sequences of increasing order for the systems CC/CL/i (reference = 3; T = 38 °C; c (guest) = 0.06 mol/1).

The numerical values of ρ and η depend on the choice of the molecule-fixed coordinate system. The largest value of ρ results if g^{o}_{ij33} is given in its system of principal axes (indicated by ρ^*, η^*)[7,8] in which X_{ij} is not necessarily diagonal. For any other coordinate system ρ and η can be expressed by a linear combination of $\rho = A\rho^* + B\eta^*$ and $\eta = A'\rho^* + B'\eta^*$ where A,B, A', and B' are functions of the elements a_{ij}. From this point of view the relative order parameter of eq. (7) can be interpreted as

$$r = \hat{\rho}_{\underline{i}} / \hat{\rho}_{\underline{3}} \tag{9}$$

with a "pseudo"-orientation axis which is now a function of the spectroscopic constant Q and, therefore, depends on the method used.

For the results described here it should be guaranteed that this "pseudo"-orientation axis is independent of the type of the molecule. For r_H this is obvious because the investigated molecules are CC and CL in all cases. Since the CD and UV spectroscopy used depends at first on the properties of the enone chromophore which is equal for $\underline{1}$ to $\underline{11}$[4] this assumption should be fulfilled for the guest, too.

DISCUSSION

The relative order parameter $r_G(\underline{i})$ of the guest molecules strongly changes with an alteration in the molecular structure of the guests. I.e. small variation of the substituents in 11α- or 17β-position causes large differences in the order parameter. Furthermore the order parameters of the host varies with the structure of the guest dissolved in CC/CL. In view of the theory of Sackmann et al.[9] $r_G(\underline{i})$ and $r_G(\underline{i})/r_H(\underline{i})$

(fig. 2) are proportional to the anisotropy of the polarizability, a condition which is fulfilled for most of the compounds analysed here. Because of conformational mobility this cannot be proven easily for all compounds 1 to 11. But 8 deviates unequivocally from this proportionality which may have its origin in a hydrogen bonding.

As shown in fig. 2 the sequences of order $r_G(\underline{i})$, $r_G(\underline{i})/r_H(\underline{i})$, and $r_H(\underline{i})$ do not coincide as a function of $\underline{i}$. For some systems (those with 1 and 8, e.g.)a high order of the guest molecule is connected with a low order of the matrix and vice verca (10, e.g.). But in general there is no proportionality and therefore the molecular properties responsible for the ordering of the guest are different from those which determine the alteration of the host order by incorporation of the guest.

REFERENCES

1. I.A. Shanks, Contemp. Phys., 23, 65 (1982)
2. e.g. R. J. Cox, Mol. Cryst. Liq. Cryst., 55, 1 (1979)
   J. Cognard and T. Hieu Phan, Mol. Cryst. Liq. Cryst., 70, 1 (1981)
3. e.g. R. Kiefer and G. Baur, Abstracts of "13. Freiburger Arbeitstagung Flüssigkristalle", Freiburg, 1983
4. J. Altschuh, R. Weiland, J.V. Kosack, and H.-G. Kuball, Ber. Bunsenges. Phys. Chem., in press (1984)
5. H.-G. Kuball and J. Altschuh, Mol.Phys., 47, 973 (1982)
6. H.-G. Kuball, J. Altschuh, and A. Schönhofer, Chem. Phys., 49, 247 (1980)
7. H.-G. Kuball, R. Weiland, V. Dolle, and A. Schönhofer, in preparation
8. H.-D. Schwaben, R. Weiland, V. Dolle, A. Strauss, P. Kau, J. Altschuh, and H.-G. Kuball, Mol. Cryst. Liq. Cryst., this issue
9. E. Sackmann and H. Möhwald, Chem. Phys. Lett., 12, 467 (1972)
   E. Sackmann, P. Krebs, H.U. Rega, J. Voss, and H. Möhwald, Mol. Cryst. Liq. Cryst., 24, 283 (1973)