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

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Version of record first published: 20 Apr 2011.

To cite this article: Ronald Y. Dong & Edward T. Samulski (1982): On The Orientational Ordering of Flexible Mesogenic Molecules, Molecular Crystals and Liquid Crystals, 82:3, 73-79

To link to this article: http://dx.doi.org/10.1080/01406568208070163

Mol. Cryst. Liq. Cryst. Vol. 82 (Letters), pp. 73-79
0140-6566/82/8203-0073$06.50/0

Printed in the United States of America

ON THE ORIENTATIONAL ORDERING OF FLEXIBLE MESOGENIC MOLECULES

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(Submitted for Publication March 22, 1982)

ABSTRACT
A general discussion of orientational ordering of mesogenic molecules with conformational flexibility is presented. It is emphasized that internal conformational and external reorientation motions can be separated in a local frame in which a local order tensor of a rigid subunit is well-defined. The local order tensor may be diagonal and its temperature dependence can therefore be compared with the molecular field theory of rigid molecules.

Various experimental methods[1] have been used in the past to examine orientational ordering of mesogenic molecules in uniaxial liquid crystals. All the methods fall into one of two categories - those that measure the macroscopic order parameters from bulk anisotropic molecular property such as the diamagnetic susceptibility, refractive index and dielectric permittivity, and those that measure directly the microscopic order parameters based on anisotropic properties of individual molecules. Those in the first category can also determine, to within a proportional constant, the microscopic order parameter which appears to agree with those obtained by the second category for molecules that can be approximated as hard rods. However a majority of these methods measures a single motionally-averaged component of an anisotropic

second rank tensor A describing a molecular property, $A_{||}$ (along the uniaxial direction (the director) of the molecular order in the mesophase). The average can be done over an ensemble of molecules having all possible conformational states and molecular orientations, provided that these motional processes are fast on the time scale of the particular experiment. The internal conformational changes result from nonrigid mesogenic molecules having many internal degrees of freedom. The molecular orientations are described by a singlet orientational distribution function and other distributions which are not easily extracted from the experimental data. It is difficult to obtain from a single value of $A_{||}$ quantitative information on the orientational order unless a model is available to account for the orientational ordering of each rigid conformation of the molecule. Tests of such a model has been facilitated by measuring several independent values of $A_{||}$ from different parts of the nonrigid molecule with deuterium NMR spectroscopy.

In the absence of a suitable model, it was assumed previously that the molecular orientation is independent of molecular conformation. This assumption leads to a characterization of the whole molecule by a single orientational order matrix. In fact, the order matrix $S_{\alpha\beta}$ measured the order of an ill-defined average conformation of the molecule. If one further assumes the average conformation is temperature independent, the temperature dependence[2] of S can be obtained. The measured $A_{||}$ is given in this case by

$$A_{||} = A_o + \frac{2}{3} \sum_{\alpha,\beta}^{a,b,c} \langle A_{\alpha\beta} \rangle S_{\alpha\beta} \qquad (1)$$

where A_o is one third of the trace of A (A_o = 0 for dipolar and quadrupolar interactions) and the angular brackets denote a molecular conformational average, provided that one can pick a molecular fixed frame (a,b,c) such that S is independent of conformation. This separation of internal and reorientational motions was recently discussed[3]. Using

symmetry to pick a frame so that S is independent of conformation is only possible for small molecules such as biphenyl and benzaldehyde dissolved in nematic solvent. This is obviously difficult if not impossible to do in liquid crystal molecules because of the numerous conformations the molecule can have. In addition the conformations are usually not related by symmetry operations. On the other hand, how does one find the average molecular conformation on the NMR time scale for which one can define $\tilde{S}$?

Recently Emsley and Luckhurst[4] have employed standard equilibrium statistical mechanics to evaluate $A_{||}$ in uniaxial liquid crystals. One basic assumption used is to express the potential energy, $U(\phi,\Omega)$, of a single molecule averaged over the coordinates of its neighbors as

$$U(\phi,\Omega) = U_{int}(\phi) + U_{ext}(\phi,\Omega)$$

where the internal energy U_{int} depends only upon the conformation $\{\phi\}$ and the external energy U_{ext} depends upon both $\{\phi\}$ and orientation (Ω) of the director in the molecular fixed frame. This allows one to decouple the internal conformational changes and the molecular reorientations. Now if $U_{ext}(\phi,\Omega)$ is independent of conformation $\{\phi\}$, one gets eq. (1), otherwise the following general expression

$$A_{||} = A_o + \frac{2}{3} \sum_{\alpha,\beta} \langle A_{\alpha\beta} S_{\alpha\beta} \rangle \qquad (2)$$

must be used. It should be noted, however, that separation of[5] conformational average of $\tilde{A}$ and $\tilde{S}$ in eq. (2) is always possible in a local frame attached to the i^{th} rigid subunit in which $A_{\alpha\beta}$ is independent of molecular conformation. In this case, one has a local order parameters $S^i_{\alpha\beta}$ of the i^{th} rigid subunit. $S^i_{\alpha\beta}$ may be directly measured by NMR provided that enough (quadrupole and dipolar) interactions are determined. There are in general five independent components in this traceless local order tensor. It should

also be noted that the S^i are not related to each other in a simple way and cannot be related to an average order tensor of the entire molecule unless one can define an averaged molecular structure.

For dipolar or quadrupolar interaction of the i^{th} rigid subunit, eq. (2) can be written as

$$A^i_{||} = \frac{2}{3} \sum_{\{\phi\}} \sum_{\alpha,\beta}^{X,Y,Z} P\{\phi\}\, A^i_{\alpha\beta}\{\phi\}\, S_{\alpha\beta}\{\phi\} \qquad (3)$$

where $P\{\phi\}$ is the probability that the molecule is in the conformation $\{\phi\}$ irrespective of its orientation Ω; $A^i_{\alpha\beta}\{\phi\}$ is the interaction tensor in the molecular fixed (X,Y,Z) frame when the molecule is in the $\{\phi\}$ conformation and $S_{\alpha\beta}\{\phi\}$ is given below to describe the ordering of individual conformations of the entire molecule

$$S_{\alpha\beta}\{\phi\} = \frac{1}{2} Q^{-1}\{\phi\} \int d\Omega [3\ell_\alpha(\phi,\Omega)\ell_\beta(\phi,\Omega) - \delta_{\alpha\beta}]$$

$$\times \exp [-U_{ext}(\phi,\Omega)/kT] \qquad (4)$$

with

$$Q\{\phi\} = \int d\Omega \exp [-U_{ext}(\phi,\Omega)/kT]$$

and $\ell_\alpha(\phi,\Omega)$ is the direction cosine that axis α in the $\{\phi\}$ conformation makes with the director. The distribution of molecules among various conformational states depends on temperature through $P\{\phi\}$ since

$$P\{\phi\} = Z^{-1} \exp [-U_{int}\{\phi\}/kT]$$

where

$$Z = \sum_{\{\phi\}} \exp [-U_{int}\{\phi\}/kT]$$

An explicit expression[5] of $U_{int}\{\phi\}$ is available to calculate $P\{\phi\}$. It is however more convenient to describe

the interaction tensor of the i^{th} rigid subunit in a local (1,2,3) frame since its elements are then independent of $\{\phi\}$. Consequently eq. (3) becomes[5,6]

$$A^i_{||} = \frac{2}{3} \sum_{\alpha,\beta}^{1,2,3} A^i_{\alpha\beta} S^i_{\alpha\beta} \tag{5}$$

where the local ordering matrix $S^i_{\alpha\beta}$ is

$$S^i_{\alpha\beta} = \sum_{\{\phi\}} P\{\phi\} s^i_{\alpha\beta}\{\phi\} \tag{6}$$

with $s^i_{\alpha\beta}\{\phi\}$ being the ordering matrix of the i^{th} rigid subunit in the $\{\phi\}$ conformation. It is obtained by transforming $S_{\alpha\beta}\{\phi\}$ of the entire molecule through

$$s^i_{\gamma\delta}\{\phi\} = \sum_{\alpha,\beta}^{X,Y,Z} \ell^i_{\gamma\alpha}\{\phi\} S_{\alpha\beta}\{\phi\} \ell^i_{\delta\beta}\{\phi\} \tag{7}$$

where $\ell^i_{\gamma\alpha}\{\phi\}$ is the direction cosine between γ axis of the local frame and α axis of the (X,Y,Z) frame in the $\{\phi\}$ conformation. (It should be noted that the (X,Y,Z) frame may be different for each conformation.) Now eq. (5) can be used to account for the quadrupolar splittings in liquid crystals provided that $S^i_{\alpha\beta}$ is known. Recently a scheme[5] was proposed to evaluate $S^i_{\alpha\beta}$ in liquid crystals with the assumption that the average orientation of a conformation depends on the shape anisotropy of the molecule as prescribed by its moment of inertia tensor. $S^i_{\alpha\beta}$ is varied in eq. (5) to fit the experimental quadrupolar splitting $\Delta\nu_i$ through[5] $U_{int}\{\phi\}$ in $P\{\phi\}$. For a CD_2 group in the alkyl chain of nCB (4-n-alkyl-4'-cyanobiphenyl) with the 3-axis perpendicular to the CD_2 plane, the 2-axis bisecting the angle $\angle$DCD and the 1-axis along the DD vector, S^i_{11}, S^i_{22}, S^i_{33} and S^i_{23} are non-zero, while S^i_{12} and S^i_{13} are zero by symmetry. For the phenyl ring in nCB, S^i should be diagonal

(in a local frame with the 3-axis along the para axis, the 2-axis perpendicular to the ring) due to local symmetry and has been measured directly in 5CB by Emsley et al[6]. Any model that describes the orientational ordering of each conformation should therefore yield[5] a diagonal $\tilde{S}^i$ for the ring in nCB.

There is however, no single ordering tensor for the entire molecule because of conformational changes which imply that each rigid conformation must be described by its own ordering matrix. $\tilde{S}^i$ is well defined and can be obtained[5] from models which relate the orientation of each conformation to, for example, the molecular polarizability tensor or the moment of inertia tensor of the entire molecule. The temperature dependence of $\tilde{S}^i$ can be studied if $\tilde{S}^i$ happens to be diagonal. Furthermore the elements of $\tilde{S}^i$ represent ordering of a rigid subunit of the molecule and can be compared with the mean field predictions based on a rigid biaxial molecular model[7].

In conclusion, $U_{ext}(\phi,\Omega)$ of liquid crystals cannot be independent of $\{\phi\}$ in general. The separation of internal conformational and reorientational motions can always be achieved in a local frame in which a local order tensor $\tilde{S}^i$ is defined. Now either $\tilde{S}^i$ can be measured directly by experiments or calculated as a weighted average of ordering matrices $S_{\alpha\beta}\{\phi\}$ which describe the ordering of individual conformations of the whole molecule. It must be emphasized that $\tilde{S}^i$ reflects the orientation ordering of the whole molecule albeit in a complex way.

Acknowledgment

The financial support of the Natural Sciences and Engineering Council of Canada (R.Y. Dong) and the National Institute of Health (E.T. Samulski) is gratefully acknowledged.

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