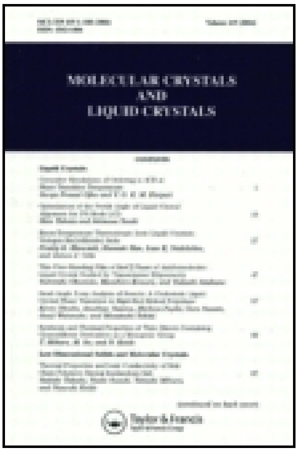

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Maximum Entropy Rotameric Distribution of Ethoxybenzene Dissolved in Liquid Crystals

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To cite this article: Donata Catalano , Lorenzo Di Bari & Carlo Alberto Veracini (1992): Maximum Entropy Rotameric Distribution of Ethoxybenzene Dissolved in Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 212:1, 155-162

To link to this article: http://dx.doi.org/10.1080/10587259208037255

Mol. Cryst. Liq. Cryst. 1992, Vol. 212, pp. 155–162
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Printed in the United States of America

MAXIMUM ENTROPY ROTAMERIC DISTRIBUTION OF ETHOXYBENZENE DISSOLVED IN LIQUID CRYSTALS

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(*Received March 11, 1991*)

ABSTRACT

The analysis of interproton dipolar couplings derived by ^{1}H-NMR spectra of molecules dissolved in partially oriented nematic solvents (LX-NMR) is a powerful tool for accurate structure determination in liquid phase.

A characterization of the distribution of the internal variables in non-rigid molecules has been one of the central goals of LX-NMR. This kind of study appears particularly relevant when considering that the mesogens themselves are often composed of molecules with one or several internal degrees of freedom.

The application of the principle of Maximum Entropy (ME) has been shown able to give the least biased rotameric distribution for one internal degree of freedom. This method is now extended to the problem of two internal rotations and applied to analyse the dipolar couplings of ethoxybenzene. A bidimensional probability distribution is thus obtained, that is in agreement with preliminary findings of a *ab initio* calculation on the molecule.

Keywords: rotameric distribution; LX-NMR data analysis, ethoxy benzene's internal rotations; maximum entropy rotameric distribution

INTRODUCTION

In recent years there has been a large and wide interest in conformational studies of non-rigid molecules in liquid phases. One of the most accurate techniques for structural determinations of molecules in solution is the so-called LX NMR, which uses the dipolar couplings between magnetically active nuclei of partially oriented molecules dissolved in liquid crystalline solvents.[1]

In spite of the formidable difficulty of analysing LX NMR spectra of molecules with more than 7-8 protons, there has been a constant effort in acquiring data on biphenyls from the one hand and on alkyl- or alkoxy- phenyls on the other.[2,3] One of the main reasons is that these classes of molecules almost invariably characterize the cores of mesogenes and the study of the flexibility of the cores seems crucial in understanding the physical properties and the structure of mesomorphic phases.

The information contained in the dipolar couplings is rather directly and unambiguously related to internuclear distances and angles for rigid molecules,[1] but there is still some controversy when approaching flexible ones. This is due to the fact that the observed quantities are averages over the ensemble of molecules and over times long compared to the intramolecular rearrangements under investigation.[4]

Only the molecules in the lowest energy level or in significantly populated local minima can contribute to the the observed dipolar couplings, thus it is not possible to study energy barriers of more than 1-2 Kcal/mol or to explore local potential maxima.

Furthermore it is widely accepted that conformation and orientation are not independent, which makes the situation even more complicated.[4]

The singlet distribution of a non rigid molecule has to be written as $P(\Omega,\chi)$,[5] where Ω represents the orientational (external) variables and χ the internal degrees of freedom; it is not allowed to partition $P(\Omega,\chi)$ into the product $P(\Omega)P(\chi)$.

$P(\Omega,\chi)$ is the direct consequence of a conformational-orientational potential, whose shape is not known and there is no definite indication of a completely satisfying model.

It is possible to recognize at least two main distinct attitudes to overcome this problem. Firstly one can seek a single-conformation solution (we shall call this the SC approach), which in fact amounts to treating the molecule as if it were rigid, optimising the internal degrees of freedom but loosing any hope in the assessment of the conformer distribution.

Secondly one can assume a shape of the internal-orientational potential and see how does this model fit the experimental data, i.e. the dipolar couplings. A rotameric distribution can be derived in this case, which to some extent depends on the assumptions introduced. Of course there has been a number of proposals in this sense, but the only one that we shall discuss below is the so-called additive potential (AP),[6, 7] which can be regarded as a sort of extension of the mean-field theory to non-rigid molecules.

Both these approaches in several occasions have shown to fit well to the experimental data, indicating that the same sets of dipolar couplings are compatible with different potentials. In fact the SC can be regarded as an extreme assumption of the shape of the conformer distribution, that is identified to a δ function.

THE MAXIMUM ENTROPY APPROACH

General theory

An alternative approach was proposed some time ago,[8] which makes use of the Maximum Entropy principle as a method for sorting the probability distributions that are compatible with (i.e. that fit well) the experimental data on the basis of a probabilistic consideration. The number of ways a probability distribution has to be realised is connected to a functional that, in analogy with statistical mechanics, is called Entropy. For our conformational-orientational problem, we can say that a $P(\Omega,\chi)$ has an entropy S defined as

$$S = -\int P(\Omega,\chi) \ln P(\Omega,\chi)\, d\Omega d\chi. \qquad (1)$$

If one has no *a priori* reason for preferring a specific $P(\Omega,\chi)$, provided it reproduces the experimental data, then the best choice is $P_{m.e.}(\Omega,\chi)$ which maximises S as defined in Eq. 1. In fact this distribution has the largest number of possible realizations and it is the *least biased* in the sense that it does not need the intervention of *a priori* knowledge

All the probability distributions compatible with the experimental data, must reproduce the observed dipolar couplings T_{ij}^{exp} for any spin pair (i,j). If we call $T_{ij}(\Omega,\chi)$ the magnitude of the z- component of the dipolar interaction between i and j when the molecule is oriented as defined by Ω and has a conformation described by χ, we can write the following condition:

$$\int P(\Omega,\chi)\, T_{ij}(\Omega,\chi)\, d\Omega d\chi = T_{ij}^{exp}. \qquad (2)$$

Together with normalization, a set of equations like Eq. 2 for all the observed *independent* couplings, constitutes a set of constraints for *any* probability distribution that ensures the reproduction of the experimental data. The solution to the Maximum Entropy problem of Eq. 1, is then the search for the stationary point of S under the constraints of Eq. 2. The standard mathematical procedure for this kind of problem consists in the introduction of Lagrange multipliers λ_{ij} associated, for each independent coupling T_{ij}, to an equation like Eq. 2. This results in the following functional form for $P_{m.e.}(\Omega,\chi)$

$$P_{m.e.}(\Omega,\chi) = \frac{1}{Z} \exp\left[-\sum_{ij} \lambda_{ij}\, T_{ij}(\Omega,\chi)\right], \qquad (3)$$

where $Z=\int P_{m.e.}(\Omega,\chi) d\Omega d\chi$ ensures the normalization of $P_{m.e.}(\Omega,\chi)$.

The correct values assumed by the parameters λ_{ij} is found by a non-linear fitting of the experimental data.

The rotameric distribution can be obtained from $P_{m.e.}(\Omega,\chi)$ by integration over the external variables Ω, which gives:

$$P_{m.e.}(\chi) = \int P_{m.e.}(\Omega,\chi) d\Omega. \qquad (4)$$

We did not specify so far the nature and the number of the internal degrees of freedom represented by χ; therefore the result of eq. (4) must be regarded as general for any set of χ's.

The problem of two internal rotations

A number of cases has been analysed elsewhere for one internal rotation in biphenyl-like molecules,[9] showing that the results of the ME approach generally are in good agreement with the expectations on the basis of theoretical calculations and usually contain (in the sense that are more spread) both SC and AP results.

From the point of view of theory, the extension to two internal rotations is straightforward, whereas it has deep and serious implications both for practical calculations and for the comparison to the AP results.

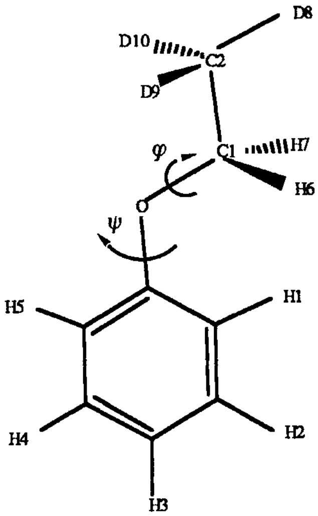
The first problem resides mainly in the CPU-time needed for optimizing the set of Lagrange multipliers λ_{ij}. As we saw above they are determined by a least squares fitting of the experimental dipolar copling through eq. (2). For two internal degrees of freedom, this involves a quadruple integration, over two Euler angles, defining the orientation in the cylindrical nematic phase and over the two internal variables. The number of points required for an accurate sampling of $P(\Omega,\chi)$ largely increases with respect to the case of one internal rotation, which renders mandatory to speed up the calculations.

The second point is more subtle. In fact the AP approach consists in the assumption of a shape for the conformational orientational potential but does not give hints to the problem of the correlation of two internal variables, that undoubtedly are not disjoint.

ME ANALYSIS OF DIPOLAR COUPLINGS IN ETHOXYBENZENE-d3

The analysis of ethoxybenzene is particularly relevant as this molecule can be regarded as the prototype a whole class of liquid crystals. In fact the molecules containing the alkoxybenzene group often exhibit a smectic C phase, provided there is a possibility of smectic polymorphism. On the contrary the analogous molecules where the oxygen has been substituted by a methylene (alkyl-benzenes) give rise to smectic A phases.[10,11] Interestingly, when both groups are present on either sides of the aromatic ring a smectic A- smectic C transition is observed. This seems to indicate that a careful analysis of the connection between chain and ring is desirable.

We re-examine the set of thirteen dipolar couplings observed for ethoxybenzene-d3 reported in literature and already analysed by means of the AP[2, 6] and SC[12] approach.



Ethoxybenzene-d3

For this molecule there are two internal rotations, one around the ring-O bond (we shall call the relevant angle ψ) and the other around the O-C1 bond (described by the angle φ). It is assumed that ψ vanishes when C1 lies on the plane of the aromatic ring and φ when the C2 lies on the plane defined by the ether bond.

The AP and SC analyses of the same set of data gave two results which are directly comparable, as the same number of fitting parameters has been used in the two approach. The main difference consists in the fact that the AP has been applied to the rotation described by φ only, assuming that $\psi=0$ or π, like in solid phase. This assumption has been discussed at length by Gallard and Volino, who stressed the fact that the two potential barriers for the rotations around φ and ψ should be comparable. On the other hand the arguments in favour of the SC postulate are not completely satisfactory, since the importance of this kind of molecules resides in the big flexibility of their structure. In the context of this open discussion it appeared particularly attractive to pursue with the ME approach in spite of the computational difficulties.

In ethoxybenzene there are 13 dipolar couplings we can choose a set of 9 λ_{ij} to describe the orientation and the conformation of the molecule:

$$\{ \lambda_{12}, \lambda_{15}, \lambda_{16}, \lambda_{18}, \lambda_{26}, \lambda_{28}, \lambda_{36}, \lambda_{67}, \lambda_{68} \}$$

λ_{12} and λ_{15} define the orientation of the phenylic moiety, that has a C_{2v} local symmetry and therefore has two independent components of the ordering tensor. λ_{67} and λ_{68} are associated with dipolar couplings between nuclei that lie on the alkylic moiety; as shown by Zannoni[5] they contain the information about the ordering of this fragment relative to the ring, which is also dependent on the rotameric distribution. λ_{16}, λ_{18}, λ_{26}, λ_{28} and λ_{36} are purely inter-fragment and participate in the assessment of $P(\varphi,\psi)$.

This set of parameters allows a good fitting of the experimental dipolar couplings, starting with the same geometry as in ref. 12 for the two "rigid" component fragments (on the "rigidity" of the ethylic group see, for example, ref. 12), see Tab I. Perhaps a slightly different choice of the starting structure would give an even better reproduction of the experimental data (the largest residuals involve only couplings between protons on the ring) but, at least at this stage, we prefer to leave this for the sake of a sounder comparison. It is worth noticing that ME approach requires a smaller number of parameters that both SC and AP.

TABLE I

Experimental and calculated dipolar couplings for ethoxybenzene d3, take from ref. 2. As in ref. 12 we choose a symmetric ring geometry , therefore $\langle T_{15}\rangle = (T_{15} + T_{24})/2$

	T_{ij} /Hz	
i, j	observed	calculated
1, 2	−2806.52	−2803.68
1, 3	−358.78	−377.28
1, 4	−6.56	−12.37
⟨1, 5⟩	163.38	168.93
1, 6	−1202.17	−1202.17
1, 8	−45.27	−45.27
2, 3	−69.35	−68.92
2, 6	−241.77	−241.78
2, 8	−17.98	−17.75
3, 6	−168.48	−168.46
3, 8	−14.16	−14.64
6, 7	4020.81	4020.78
6, 8	−137.85	−137.86

For this molecule $P_{m.e.}(\Omega,\chi)$ is a function of four variables, namely the second and the third Euler angles that describe the orientation of the molecule in the cylindric phase of the nematic solvent (I52) and the two internal angles φ and ψ. Once integrated over the external variables, it gives a function $P_{m.e.}(\varphi,\psi)$ that describes the probability distribution of the conformers. This two-dimensional map can be represented by the contour plot of Fig. 1.

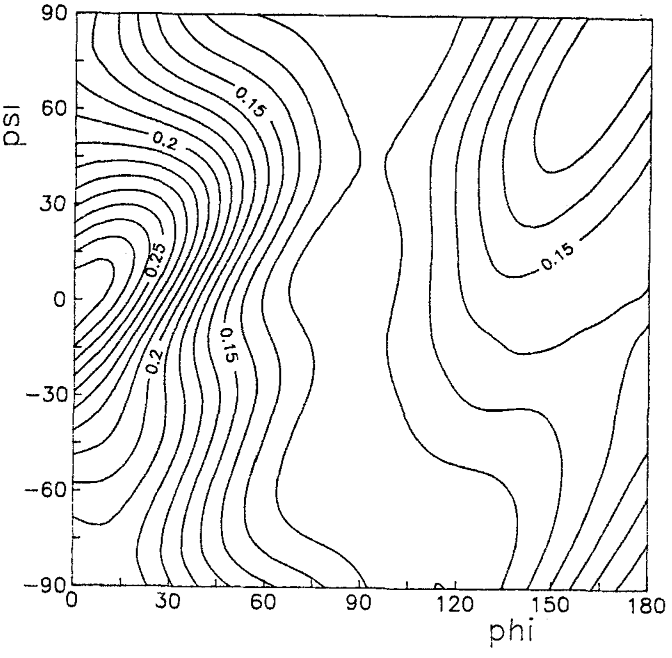


FIGURE 1 Contour plot of $P_{m.e.}(\varphi,\psi)$ for ethoxybenzene-d3.

DISCUSSION

The map of Fig. 1 summarizes the result of the first two-dimensional ME rotameric distribution. On the basis of the experience of one rotation in biphenyl-like molecule, we can expect that $P_{m.e.}(\varphi,\psi)$ is in fact more spread than the "true" distribution, i.e. the potential barriers appear to be slightly underestimated. This means that the two angles are rather confined in the region $-30 \leq \psi \leq 30°$ and $-20 \leq \varphi \leq 20°$, but still we can appreciate that ψ results fairly free to vary, in this region, whereas φ is much more confined around 0°.

The preliminary results of an *ab initio* calculation currently in progress on ethoxybenzene *in vacuo* , indicate that the most stable conformer is found for $\psi=0°$, $\varphi=0°$ and that the rotation described by ψ is not very hindered, whereas φ is much more restrained to small values.[13] All this seems in very good agreement with the present findings

The ME result can be compared with those derived through SC and AP approach.

The single conformation finds $\varphi=39.18°$ and $\psi=-22.75°$, but this method does not account for any freedom of rotation around these bonds and both ME and the theoretical calculation seem to indicate that the flexibility for this molecule is rather large.

In the AP approach the sum of the first seven Fourier terms for V(φ) was taken into account, while keeping $\psi=0°$. V(φ) thus obtained features a deep minimum for $\varphi=0°$ and local minima for $\varphi=\pm120°$, corresponding to the *gauche* conformations. The assumption of the co-planarity of the ether bond and the ring seems unrealistic on the basis of $P_{m.e.}(\varphi,\psi)$, anyway, if we take a section of $P_{m.e.}(\varphi,\psi)$ at $\psi=0$ we cannot exclude the existence of a *gauce* conformation. Seemingly, the potential barriers in V(φ) of AP are to be taken with some caution, as they imply the observation of states with very high energy that, at room temperature are not to be expected to be populated.

CONLUSIONS

We have introduced a maximum entropy distribution for to internal variables in ethoxybenzene. The resulting $P_{m.e.}(\varphi,\psi)$ is in good agreement with expectations on the basis of theoretical calculation. A comparison with a single-conformation and an additive potential solutions of the same problem indicate that it is not realistic to assume the he co-planarity of the ether and the ring and that both rotations are important. Study is in progress on substituted ethoxybenzenes, that are more oriented in the nematic phase, on the one hand, and on a thorough investigation of the *ab initio* potential, on the other.

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