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The structure of substituted biphenyls as studied by proton NMR in nematic solvents

Single conformation model versus maximum entropy analysis

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Published [11, 12] proton nuclear magnetic resonance data for two substituted biphenyl molecules dissolved in nematic solvents are analysed in terms of the single conformation model and compared with the results of the maximum entropy analysis of [11]. It is shown that (i) this model, in which the number of adjustable parameters is less than the number of data, can describe very well the data for both molecules and (ii) the results of the maximum entropy analysis provide global support for this model. It is argued that the ultimate support of the single conformation model would be that introduction of a sufficiently large number of additional data in the maximum entropy analysis leads to a distribution for the dihedral angle between the two phenyl rings with two symmetrical very sharp peaks.

1. Introduction

The description of non-rigid molecules in fluid phases has attracted considerable attention for at least two decades. The development of NMR techniques now allows us to produce accurate data from such molecules in (fluid) anisotropic media [1–3], data which are highly relevant in this field of research. Surprisingly, there is not yet a consensus on how these data should be analysed, and disputes and controversies have plagued the literature for many years. The most typical example is probably that of the nematic phase of 4-N-pentyl-4′-cyanobiphenyl (5CB) for which a very large amount of data is available (maybe the largest at present for a small molecule), and for which three different models have been proposed so far [4–6]. Although the various authors criticize one another, all of these models are based on the rotameric isomeric state scheme, in which the pentyl chain is assumed to exist in $3^3 = 27$ conformations, as in the isolated molecule. These models correspond to a gas-like picture of a liquid, in which an isotropic phase is identified to a gas phase, and a fluid anisotropic phase to a biased gas phase.

In several papers [7–10], we have argued that if such a picture is acceptable to describe macroscopic (statistical) properties, it is a very poor description of molecular properties, and that a solid-like picture in which the molecules exist in essentially one conformation, as in the solid phase, is preferable. The main arguments to support this view lie in the fact that (i) the density of a liquid is very close to that of the solid existing at lower temperature and (ii) significant diffuse scattering exists in a liquid at nearly the same place as that of the Bragg peaks of the solid, suggesting comparable molecular

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structure and arrangement in both phases. Thus, the local disorder that exists at the molecular scale in a liquid must be such that it satisfies these two requirements. This has led to the single conformation model in which the only allowed large amplitude internal motions (those which produce significant averaging of the magnetic interactions) are symmetry operations such as π-flips of phenyl rings, methyl group rotation and exchange with the mirror image conformation (dynamical racemization). Clearly if additional internal disorder exists in the solid phase, such as end-chain motion, this disorder survives in the liquid phase. Another consequence of the solid-like picture of a liquid is that there is no essential difference between isotropic or anisotropic phases at the molecular scale (the difference is only macroscopic), so that there should not be any significant contribution of the molecular conformations to the clearing transition enthalpies and entropies, a prediction which seems to be supported by experiment (a dimer liquid crystal [9], 5CB and 8CB [5]).

Recently, a different approach has been proposed to analyse NMR data of substituted biphenyl molecules dissolved in liquid crystals, based on the maximum entropy principle [11]. From a purely operational viewpoint, the approach may be considered as a particular many conformation model, in the sense that the internal variables which describe the conformations are assumed to be distributed. In molecules as simple as those considered in [11], there is only one internal variable, namely the dihedral angle, ϕ, between the rings. Each value of ϕ corresponds to a different conformation, and the difference between the possible many conformation models lies in assumptions about the relation between conformation and orientation. In the maximum entropy analysis, no assumptions of this kind are made, but the least biased (i.e. the flattest and broadest) distribution of the statistical variables (conformational and orientational) is sought, which is compatible with the data. Clearly, this distribution cannot be the true distribution since it depends on the nature and number of the data. However, it is expected that the maximum entropy distribution will tend towards the true one in the limit of a very large amount of data. Thus the ultimate support for the single conformation model would be that, in this limit, the maximum entropy distribution, averaged over the orientational variables, tends towards a (single) sharp peak.

The purpose of this paper is to test these ideas with two substituted biphenyl molecules considered in [11].

2. The NMR data of two substituted biphenyl compounds, and analysis in terms of the single conformation model

2.1. *General*

We consider the proton NMR data of 4,4′-dichlorobiphenyl (DCB) dissolved in nematic I52 at three temperatures, and those of 4′-bromo-4-chloro-2,6-difluorobiphenyl (DIF) in a mixture of nematics, at one temperature. These data are published in [11] for DCB and in [12] for DIF. The structure of these two molecules is sketched in figure 1. Seven different dipole interactions for DCB and twelve different dipole interactions for DIF have been measured with high accuracy. These data are reproduced in the table. We show now that these data can be analysed in terms of the single conformation model. In order to reduce the number of adjustable parameters, it is necessary to introduce as much structural information as possible that comes from sources other than NMR. The most confident source is single crystal X-ray crystallography. The structures of solid DCB and solid DIF are not known. The closest

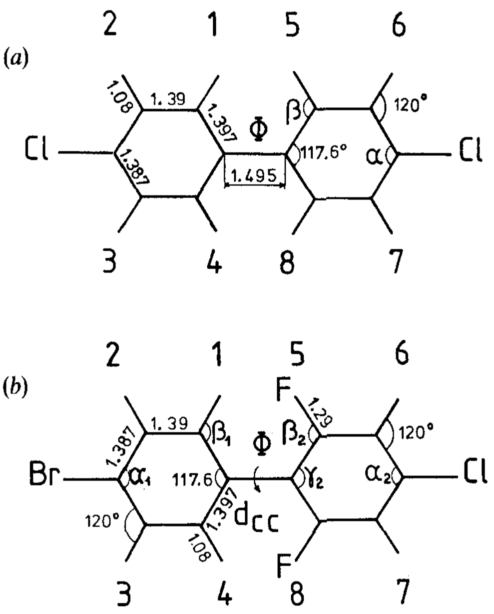

Figure 1. Sketch of the DCB (*a*) and DIF (*b*) molecules showing the labelling of the various spins *i* and the definition and values of bond distances and angles. The values quoted are those of biphenyl in the solid phase, taken from [13], and assumed to be fixed in the calculations.

Dipolar couplings, D_{ij}, as defined in [11], of 4,4-dichlorobiphenyl (DCB) dissolved in the nematic phase of I52, at three temperatures (rms error: 1·4, 2·5, 5·0 Hz at 312, 322, 332 K, respectively), and of 4′-bromo-4-chloro-2,6-difluorobiphenyl (DIF) in a mixture of EBBA and X11643 at 295 K. The observed values are taken from [11] and [12]. The calculated values are those for the single conformation model discussed in the text.

	D_{ij} Hz							
	DCB						DIF	
	312 K		322 K		332 K		295 K	
i,j	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1,2	−5374·6	−5374·7	−5167·4	−5167·4	−4922·3	−4922·3	−3770·9	−3770·9
1,3	69·5	69·1	65·0	65·0	59·6	60·1	61·2	61·2
1,4	477·4	478·1	457·0	456·7	430·5	431·4	360·5	360·6
1,5	−1908·2	−1908·3	−1820·7	−1820·6	−1720·6	−1720·6	−265·6	−265·3
1,6	−446·2	−446·7	−428·3	−429·3	−406·5	−408·7	−264·7	−264·2
2,3	479·5	479·1	456·0	457·7	432·9	432·3	360·5	360·4
2,5							−240·8	−241·7
2,6	−167·9	−164·1	−160·9	−157·8	−154·8	−150·3	−113·3	−110·5
5,6							−3157·9	−3157·8
5,7							25·1	27·8
5,8							197·8	197·7
6,7							284·3	283·2

molecule whose structure has been solved by single crystal X-ray crystallography is biphenyl [13]. This study reveals that the rings are not perfect hexagons, although the symmetry with respect to the para-axes is preserved. We have fixed the values indicated in figure 1 to the values found for biphenyl, but left some of the other angles, namely α and β in DCB and α_1, β_1, α_2, β_2 and γ_2 in DIF, as adjustable parameters within very narrow limits. Indeed it is not expected that the mean value of these angles in different molecules are exactly the same as in biphenyl. Note that these fitted angles are those for which the differences with biphenyl are presumably most significant (for example near the fluorine atoms in DIF).

The analysis was performed in the same way as with ethoxybenzene [8], to which the reader is directed for details. Here the problem is much simpler however. A frame is attached to one ring in DCB, with Oz along the para-axis and Ox in the plane of the ring. For DIF, the frame is similarly attached to the fully hydrogenated ring. We have considered the case of DCB first. This molecule has D4 symmetry, so that the principal axes of the order tensor are completely determined by symmetry. The principal axis OZ is the line along the two para-axes, that is Oz, and OX and OY lie in the two bisector planes. According to the prescriptions of our model, the only internal motions are symmetry operations, namely (uncorrelated) π-flips of the two rings around their para-axes. The exchange with the mirror image is irrelevant here because the corresponding averaging of the magnetic interactions has already been performed by the π-flips. This does not mean that such motion is absent, and probably, it actually occurs. The free parameters of the problem are the two angles α and β, the dihedral angle ϕ between the two rings and the two components T_{zz} and $T_{xx}-T_{yy}$ of the order tensor. Because of the D4 symmetry, $T_{xy}=\frac{1}{2}(T_{xx}-T_{yy})\tan(\phi)$, $T_{yz}=T_{zx}=0$. In total, there are five free parameters to be determined by seven pieces of data, a situation that is similar to that of ethoxybenzene [8]. In fact, the test is more severe here since the data exist for three temperatures, and only the two order tensor components, and the dihedral angle ϕ are allowed to vary.

The case of DIF was also examined. The symmetry is now only D2. The principal axis OZ is still along the line along the two para-axes, implying $T_{yz}=T_{zx}=0$ as for DCB, but the three other components now need to be considered as adjustable parameters. In addition to the five structural angles mentioned previously, the two other geometrical parameters are the dihedral angle ϕ (as for DCB), and the value of the CC distance between the two rings d_{CC} which could not be fixed to the value of biphenyl (1·495 Å). In total, there are ten parameters to be determined by twelve pieces of data, again a situation similar to that of ethoxybenzene [8].

2.2. *Results*

2.2.1. *DCB*

The best fitted values of the geometrical parameters are $\alpha=119{\cdot}7^\circ$, $\beta=119{\cdot}5^\circ$ and $\phi=32{\cdot}51^\circ$, $32{\cdot}62^\circ$, $32{\cdot}72^\circ$ at 312, 322, 332 K, respectively. The two components of the order tensor T_{zz} and $T_{xx}-T_{yy}$ are 0·6629 and 0·0416; 0·6374 and 0·04381; 0·6071 and 0·04656 at 312, 322 and 332 K, respectively. The values of the dipole interactions calculated with these values of the parameters are given in the table.

These results show that the molecular properties, namely the structure, but also the conformation are independent of temperature. The overall variation of ϕ of 0·2° over 20 K can indeed be considered as negligible since fits of practically the same quality are obtained by fixing this angle to the average value. In contrast, the statistical properties of the nematic phase pictured by the values of the order tensor components are strong functions of temperature.

Diagonalization of the order tensor yields the principal frame $OXYZ$ and the uniaxial and biaxial order parameters S_{ZZ} and $S_{XX}-S_{YY}$. As already mentioned, the principal planes XOZ and YOZ are the two bisector planes of the rings. With the convention that OX and OY are such that $S_{XX}-S_{YY}$ is positive (OX is less ordered than OY), ZOX is the bisector plane corresponding roughly to the plane of the molecule. The uniaxial and biaxial order parameters are: 0·6629 and 0·0489; 0·6374 and 0·0526; 0·6071 and 0·0554 at 312, 322 and 332 K, respectively (note that $S_{ZZ}=T_{zz}$ for evident reasons). It is observed that S_{ZZ} decreases and that $S_{XX}-S_{YY}$ increases slightly with increasing temperature. This result is in agreement with theory [14–16], and observed in other nematic phases for non-rigid molecules [7, 17] (this behaviour is common for rigid molecules, see, for example, [18]).

2.2.2. *DIF*

The best fitted values of the structural parameters are $\alpha_1=119{\cdot}6°$, $\beta_1=119{\cdot}5°$, $\alpha_2=119{\cdot}1°$, $\beta_2=121{\cdot}7°$, $\gamma_2=120{\cdot}7°$, $d_{CC}=1{\cdot}512$ Å. The dihedral angle ϕ is 47·80°. The values of the three order tensor components T_{zz}, $T_{xx}-T_{yy}$ and T_{xy} are 0·464, −0·004 and 0·040, respectively. The calculated values of the dipole interactions are given in the table. Diagonalization of this tensor yields the principal axes and the two order parameters. The principal plane XOZ is between the two rings as in DCB, but now very close to the plane of the fluorinated ring (at 1·29° from the fluorinated ring and 46·51° from the protonated ring: the sum is just 47·80°). The order parameters S_{ZZ} and $S_{XX}-S_{YY}$ are 0·464 and 0·080, respectively.

2.3. *Discussion*

These results show that the single conformation model is sufficient to describe satisfactorily the sets of NMR data for the two molecules considered. Indeed nothing unexpected is predicted by this model.

The values found for the angles α, β, γ are comparable to those of biphenyl, and can thus be considered as acceptable in the absence of further structural information. The fact that the distance d_{CC} in DIF is found to be slightly larger than in DCB and in biphenyl is consistent with the presence of the two bulky fluorine atoms. Thus, the structural angles and distances are very similar in all three molecules. In contrast, the conformations are different. This is not surprising since crystallographic data of other substituted biphenyls show that the angle ϕ can lie between about 10° in biphenyl [13] to values larger than 40° in cyanobiphenyl compounds [19–21], (the value for biphenyl in the gas phase is close to 45° [22]), emphasizing the importance of packing forces to determine this angle in condensed matter.

Concerning the orientational order, the most interesting result is probably the finding that the principal plane XOZ in DIF is practically the plane of the fluorinated ring. All of these results appear as reasonable support for the single conformation model for these molecules. The quality of the test is now checked with the results of the maximum entropy analysis.

3. Comparison with the maximum entropy results

In figure 2 are reproduced the distribution functions $p(\phi)$ predicted by the analysis of [11], and the distribution predicted by the single conformation model, namely two delta peaks at ϕ and $\phi+\pi$, for DCB and DIF.

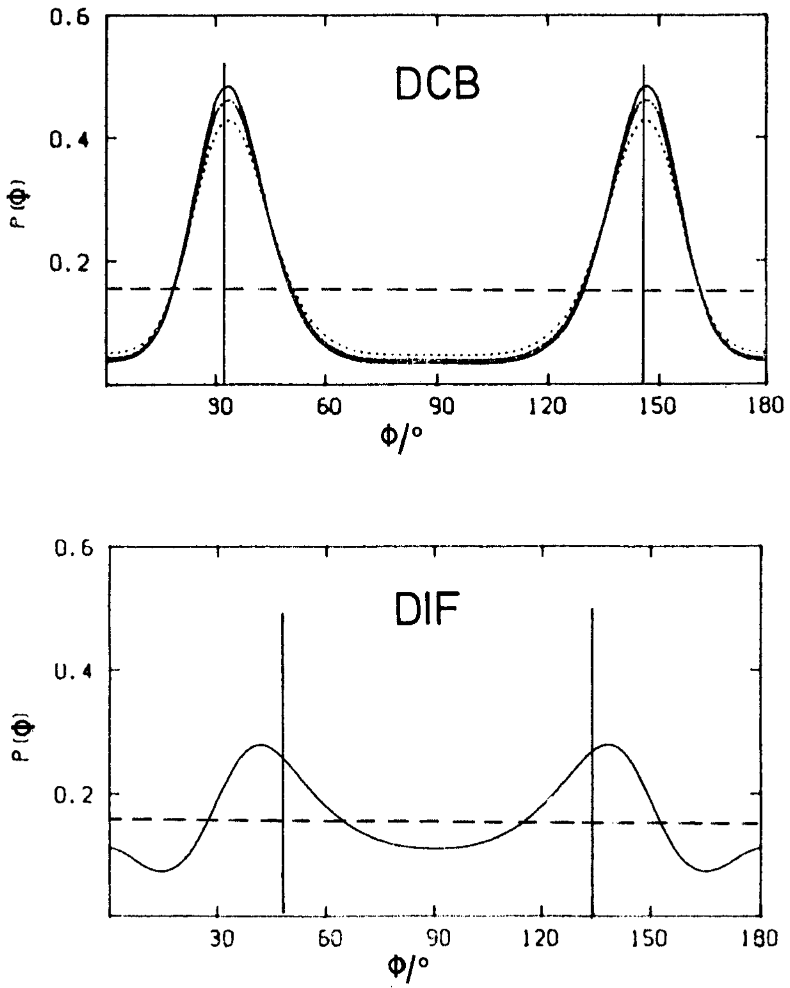

Figure 2. Probability distributions of the dihedral angle ϕ between the two phenyl rings of DCB and DIF, predicted by the maximum entropy treatment (reproduced from [11]). Note that for DCB, the width of the distribution increases as the temperature increases, i.e. as the order, picturing the amount of information, decreases (as expected). The vertical lines correspond to the single conformation model (delta peaks) and the horizontal dashed line (ordinate $1/2\pi = 0{\cdot}159\ldots$) corresponds to the uniform distribution (maximum entropy distribution in the absence of any data).

For DCB, the maximum entropy analysis appears to provide good support for the single conformation model, in the sense that it seems to exclude any conformation model with two or several conformations with very different values of the dihedral angle. The fact that the delta functions correspond to the two maxima of the distribution and are practically independent of temperature, suggests that the shape (not the height!) of the distribution is probably close to that of the true distribution (the peaks are broadened by small amplitude librational motions).

For DIF, the situation is different. The distribution $p(\phi)$ is broader, with two maxima. The main maximum is close, but not identical, to the position of the delta function, and the secondary maximum is at 0 (or π). Existence of these two maxima may mean that (i) this molecule exists in essentially two conformations, and if so, (ii) the fact that the single conformation model works well, is fortuitous. However, is is clear from steric considerations that the internal energy for a flat conformation is large in DIF [12], implying that the probability is very weak for $\phi = 0$. Thus, this secondary maximum probably does not reflect any physics, but particular features of the NMR data. This result probably also means that the amount of molecular information contained in the twelve pieces of data for DIF is less than the seven data for DCB, a situation which seems to be paradoxical. The contradiction may, however, be only apparent, because the symmetry is lower in DIF.

At this stage, it is worth noting that the maximum entropy analyses of [11] has been performed with slightly different geometries, so that, strictly speaking, the comparison cannot be made. However, because the theoretical values of the inter-ring interactions, which contain the information on $p(\phi)$, are little affected by small changes in the angles and distances, it can reasonably be expected that the maximum entropy analysis repeated with the present geometries will yield essentially the same results.

The result for DIF emphasizes the fact that the distribution does not correspond to a physical quantity, but to our degree of knowledge about the system after analysis of the corresponding data. If this degree is large, as seems to be the case for DCB, the maximum entropy distribution may be close to the true distribution. If the degree is small, as for DIF, the similarity is only rough, and incorrect conclusions may be drawn (for example the existence of flat conformers in DIF) if the basic principles of the maximum entropy analysis are not kept in mind. In this context, it would be very interesting to see how the distribution changes, if the additional piece of data, constituted by the condition that the probability of occurrence of flat conformations in very small, is introduced in the analysis.

In conclusion, it appears that modelling and the maximum entropy method are two complementary ways to analyse experimental (NMR or other) data. The latter method may possibly be a way to support some models (as is the case with the single conformation model for DCB and to a lesser extent, for DIF). or reject others. Nonetheless, the simplest manner to test models is to study their predictive character, by including more and more independent pieces of data into the analysis without increasing the number of parameters. Combination of both methods is certainly the most convincing way to establish the validity of models.

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