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A NEW MAXIMUM ENTROPY CONFORMATIONAL ANALYSIS OF BIPHENYL IN LIQUID CRYSTAL SOLUTION

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Abstract We use the maximum entropy internal order (MEIO) method to reanalyze published ^{1}HNMR dipolar couplings for biphenyl dissolved in nematic solvents allowing for geometry variations with dihedral angle ϕ. We find that all present experimental data are consistent with similar conformational distributions with a maximum at $\phi = 34 - 35°$. Little rotational–conformational coupling has been found.

The determination of the preferred conformation of biphenyl is one of the classical problems in chemical physics, possibly because it is well known that its conformation changes with the environment. The limiting situations of biphenyl in the gas phase and in the solid state are well established and correspond to an internal angle of 44° [1] and 0° [2] respectively. The case of biphenyl in solution is clearly more complex. On one hand the question is if and how the angle is affected by changing solvent. On the other hand and more stringently the problem is how to determine this delicate piece of information when only having available the limited data that is observable in a liquid after the averaging effects produced by molecular rotations. This last problem has been elegantly tackled by ^{1}HNMR experiments in liquid crystals (LXNMR) [3]. The LXNMR technique has been employed for many years but with a practical limitation in the number of proton dipolar couplings that could be determined. The situation is now improving rather substantially both by the combination of deuteration and strenuous NMR spectral analysis [4] and by the development of more sophisticated NMR experiments. Particularly interesting from this point of view are the recent multiple quantum ^{1}HNMR results of Burnell *et al.* [5].

In view of the predictable availability of a larger amount of data not only on biphenyls but also other flexible molecules, it is interesting to see if the quality of the data is now sufficient to answer some other and more detailed questions on the prototype molecule biphenyl. In practice the problem we wish to address here is the determination of the orientational–conformational distribution from these recently published data. Moreover recent [7] multiconfigurational second–order perturbation

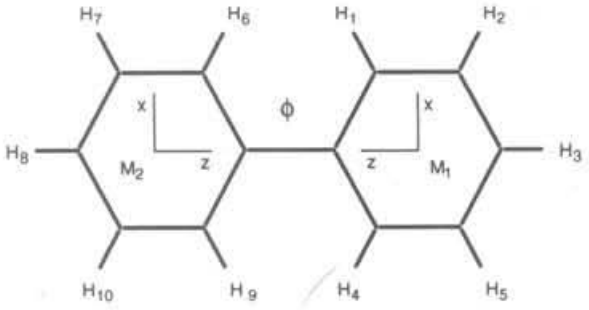

Figure 1: A pictorial sketch of biphenyl with the labelling used in ref. [5] for the ^{1}H nuclei. The dihedral angle ϕ and molecular reference frames M_1, M_2 are shown.

theory (CASPT2) ab–initio calculations have provided minimized geometries as a function of the dihedral angle between rings and we wish to allow for this geometrical effect as well. We shall use for this purpose a rather general model independent maximum entropy approach (MEIO), described in detail in [6]. This allows us to consider not only the determination of the preferred internal dihedral angle, but also to examine if this varies when the molecule has different orientations with respect to the director. Clearly if this was the case the preferred angle determined from liquid crystal analysis could not be very convincingly taken as typical of that for biphenyl in a generic fluid phase. For the same reason it is interesting to compare the results obtained for biphenyl in various solvents since some quality data are now available.

Two excellent studies of the conformational distribution of biphenyl in ordered fluid phases have been reported in the literature [4, 5]. The biphenyl ^{1}HNMR spectra were recorded from solutions in the following nematic solvents: ZLI1115 and I35 [4] and a mixture 55 wt % of ZLI1132 (Merck) in *N*-(4–ethoxybenzylidene)–4'–*n*–butylaniline (EBBA) [5]. Both groups of authors were able to solve the rather formidable task of studying the ^{1}HNMR spectrum for this 10–spin system determining the twelve symmetry independent dipolar couplings. Preliminary investigations of ^{2}HNMR [4] or of multiple quantum [5] spectra were necessary for setting up the fitting procedure of the complex ^{1}HNMR spectrum. The resulting dipolar couplings were analyzed in terms of the following models: a rigid conformer in ref. [5] and a Mean Field model with a two term Fourier conformational internal potential in refs. [4, 5] (AP model). In addition, the authors of ref. [4] also used a maximum entropy analysis, although different from the present one, and found a slight discrepancy between the two methods; the ME method found $\phi_{max} = 34°$ and the AP $\phi_{max} = 37°$. The problem of geometry dependence and of rotational–conformational coupling was not addressed explicitly.

We have presented our MEIO method elsewhere [6] and here we only summarize the essential points. The nuclear dipolar coupling D_{ij} between a pair of nuclei i, j with giromagnetic ratios γ_i, γ_j depends on the interatomic distance r_{ij} and on

		Geometry (a)				Geometry (b)			
T_I^S	Pair	t_1	t_2	t_3	t_4	t_1	t_2	t_3	t_4
1	{1,2}	84.48	4.02	8.31	0.18	79.04	8.20	9.56	0.44
2	{1,3}	1.10	0.74	0.13	1.05	1.05	0.86	0.03	0.01
3	{1,4}	0.90	5.01	0.27	0.60	0.88	4.20	1.05	0.00
4	{2,5}	0.90	5.06	0.26	0.23	0.88	4.17	1.05	0.00
5	{1,5}	0.04	1.38	0.02	0.17	0.04	1.20	0.17	0.00
6	{1,6}	9.74	0.57	89.52	0.17	15.12	6.97	77.75	0.16
7	{1,7}	0.46	0.09	0.05	96.27	0.49	0.09	0.05	98.18
8	{1,8}	0.25	0.05	0.04	0.08	0.26	0.08	0.02	0.00
9	{2,3}	1.99	83.05	1.40	0.18	2.11	74.21	10.30	0.05
10	{2,7}	0.07	0.01	0.00	1.06	0.07	0.02	0.00	1.15
11	{2,8}	0.04	0.00	0.01	0.01	0.04	0.01	0.00	0.00
12	{3,8}	0.03	0.00	0.00	0.00	0.03	0.00	0.00	0.00

Table 1: Percentage contribution of the different symmetrized couplings T_I^S to the orthogonal combinations t_I obtained using the two biphenyl geometries (a), (b) described in the text and the orthogonalization procedure of ref. [6]. The threshold for discarding eigenvalues of the overlap matrix were 10.0Hz (a) and 0.5Hz (b).

molecular geometry [6]

$$D_{ij} \equiv \sqrt{\frac{2}{3}}\langle [T_{ij}]^{2,0}_{LAB}\rangle = -\frac{h\gamma_i\gamma_j}{4\pi^2}\left\langle \frac{P_2(\cos\theta_{ij})}{r_{ij}^3}\right\rangle, \tag{1}$$

where θ_{ij} is the angle between the internuclear vector $\mathbf{r}_{ij}$ and the magnetic field direction. For a flexible molecule, r_{ij} and θ_{ij} will depend in general on the structure of the molecule and at least a subset of dipolar couplings will be modulated by configurational changes. $\langle \ldots \rangle$ indicates an average over the single particle orientational–conformational distribution. Transforming to the M_1 molecular frame placed on the first ("rigid") fragment, we have

$$\langle [T_{ij}]^{2,0}_{LAB}\rangle = \sum_{n=-2}^{2} \langle D^{2*}_{0n}(\omega)[T_{ij}]^{2,n}_{M_1}(\phi)\rangle. \tag{2}$$

where $D^2_{mn}(\omega)$ is a Wigner rotation matrix [8] depending on the molecular orientation $\omega \equiv (\alpha,\beta,\gamma)$ in the director frame. The coupling of molecular symmetry with the characteristics of the NMR experiment and its time scale will reduce the number of observable couplings to those generated by a suitable symmetrization with respect to equivalent ^{1}H pairs. For molecules such as biphenyl formed by two indistinguishable rotors we can introduce the symmetrized spherical components of dipolar couplings

$$\langle [T^{S_1}_{ij}]^{2,0}_{LAB}\rangle = \sum_{n=-2}^{2} \left\langle \frac{D^{2*}_{0n}(\omega) + e^{-in\phi}D^{2*}_{0-n}(\omega)}{2}[T_{ij}]^{2,n}_{M_1}(\phi)\right\rangle \tag{3}$$

	ZLI1132/EBBA			I35			ZLI1115		
D_I	exper.	(a)	(b)	exper.	(a)	(b)	exper.	(a)	(b)
1	-3119.66	1.79	-0.19	-4004.76	2.34	-0.20	-3173.98	1.85	-0.15
2	-392.60	-6.21	0.33	-497.01	-7.39	1.03	-404.93	-6.47	-0.02
3	194.70	2.40	-0.36	276.54	4.56	0.97	178.14	2.84	-0.04
4	194.50	1.74	-0.05	275.64	3.00	0.80	177.10	1.47	-0.61
5	0.50	-2.78	-0.91	13.69	-3.00	-0.48	-9.89	-3.04	-1.35
6	-1027.40	-0.07	0.00	-1303.23	-0.09	0.00	-1013.66	-0.08	0.00
7	-264.42	-0.93	0.04	-336.39	-1.28	0.05	-270.04	-0.97	0.07
8	-183.80	-7.84	2.36	-234.52	-9.71	3.17	-188.44	-8.34	2.00
9	-8.50	-0.17	0.17	85.58	-0.93	-0.50	-86.86	-0.16	0.32
10	-99.10	-2.94	-0.40	-126.52	-3.74	-0.48	-101.46	-3.21	-0.63
11	-76.00	-3.71	-0.55	-96.84	-4.23	-0.22	-76.74	-2.97	0.22
12	-59.50	-2.48	0.09	-76.31	-3.08	0.18	-60.52	-2.47	0.10
σ		3.68	0.81		4.64	1.11		3.82	0.79
S_{xx}		-0.123	-0.132		-0.178	-0.187		-0.113	-0.121
S_{zz}		0.378	0.397		0.489	0.509		0.385	0.404

Table 2: Symmetrized experimental ^{1}HNMR couplings $D_I = (2/3)^{1/2} T_I^S$ for biphenyl dissolved in different nematic solvents: mixture 55 wt % of ZLI1132 in EBBA [5], I35 [4] and ZLI1115 [4]. Differences between experimental and optimized MEIO values are reported in adjacent columns for both molecular geometries (a), (b) described in the text. All couplings, deviations and errors are expressed in Hz. The orientational order parameters S_{xx}, S_{zz} obtained from the MEIO analysis are also reported. All MEIO results have and estimated error of ± 1 on the last digit.

$$= \sum_{n=-2}^{2} \left\langle \frac{D_{0n}^{2*}(\omega_1) + D_{0n}^{2*}(\omega_2)}{2} [T_{ij}]_{M_1}^{2,n}(\phi) \right\rangle$$

where ω_1, ω_2 define the orientations of the M_1 and M_2 fragments (defined as in fig. 1) with respect to the laboratory frame.

The experiments in refs. [4, 5] determined 12 D_{ij}, however this large set of data can be misleading, because the information obtainable depends not on the number of D_{ij} but on the number of linearly independent combinations. As described in [6], we can identify a set of n_C orthogonalized couplings by calculating an overlap matrix $\mathbf{V}$ between the observable coupling functions, diagonalizing it and eliminating the combinations corresponding to eigenvalues smaller than a measurable threshold. The independent combinations are

$$\begin{aligned} [t_I]_{LAB}^{2,0}(\omega, \phi) &= \sum_{J=1}^{N} [T_J^S]_{LAB}^{2,0}(\omega, \phi) Z_{JI} \\ &= \sum_{n=-2}^{2} D_{0,n}^{2*}(\omega) \, [t_I]_{M_1}^{2,n}(\phi) \end{aligned} \tag{4}$$

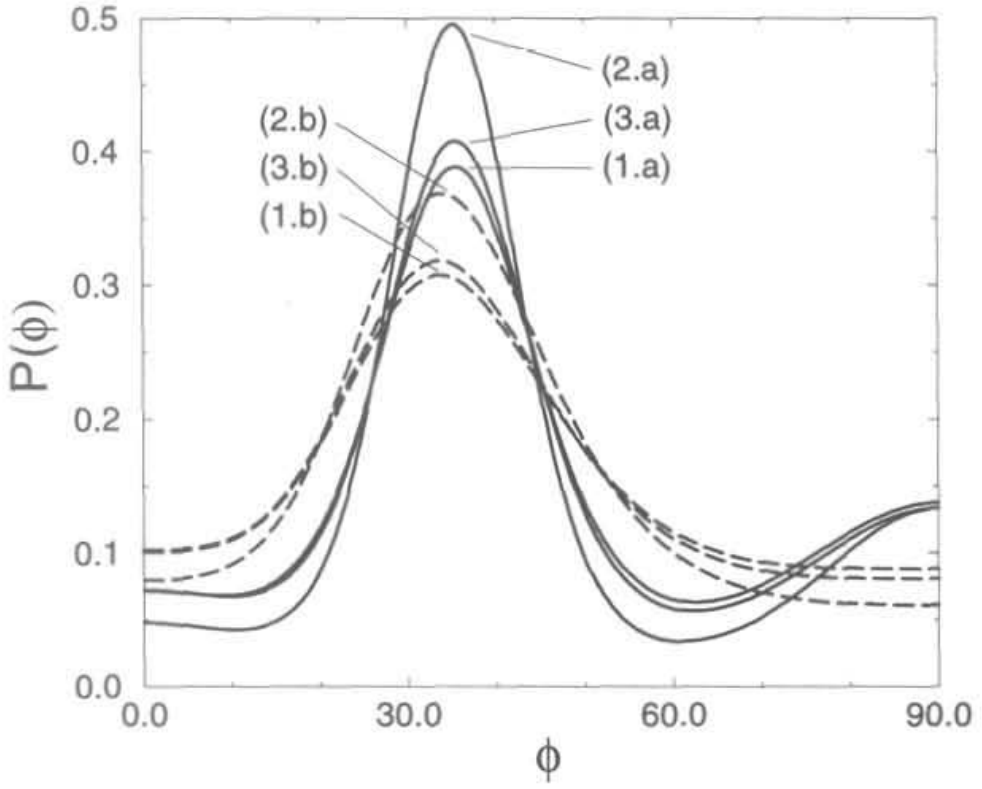

Figure 2: Conformational distribution function $P(\phi)$ for biphenyl from the MEIO maximum entropy analysis of dipolar couplings measured in ZLI1132/EBBA (1), I35 (2) and ZLI1115 (3) using the geometries (a) (solid lines) and (b) (dashed lines).

where $\mathbf{Z}$ is the matrix of eigenvectors of $\mathbf{V}$. In a similar fashion the transformation eq. 4 defines a linear combination d_I of the experimental couplings.

In Figure 1 we show a picture of biphenyl with the labelling used for the ^{1}H nuclei and the reference frames. Because of its symmetry, the conformational state of biphenyl is described in terms of a continuous dihedral angle ϕ in the range $[0, \pi/2]$. All conformational states are sterically accessible and we do not need to use any *intrinsic* conformational distribution [9]. In practice we take the reference conformation ($\phi = 0°$) as the planar one.

The effect of molecular structure has been taken into account analyzing the experimental couplings in terms of three sets of coordinates for the hydrogen nuclei. The first set of coordinates (geometry (a)) derives from CASPT2 calculations [7] of the structure of biphenyl at three conformations ($\phi = 0$, 44.34 and 90.0°). The conformational dependence for each proton coordinate was then interpolated using a three parameter formula $a\cos^4\phi + b\cos^2\phi + c$. The second set of coordinates (geometry (b)) corresponds to a rigid skeleton and has been computed using a procedure similar to that described in ref. [4]. The subset of seven couplings between nuclei whose dipolar coupling is not modulated by conformational changes has been fitted in terms of two order parameters S_{zz}, S_{xx} and five ^{1}H nuclei coordinates. The distance $r_{12} = 2.481$Å has been kept fixed. The procedure was repeated for the three

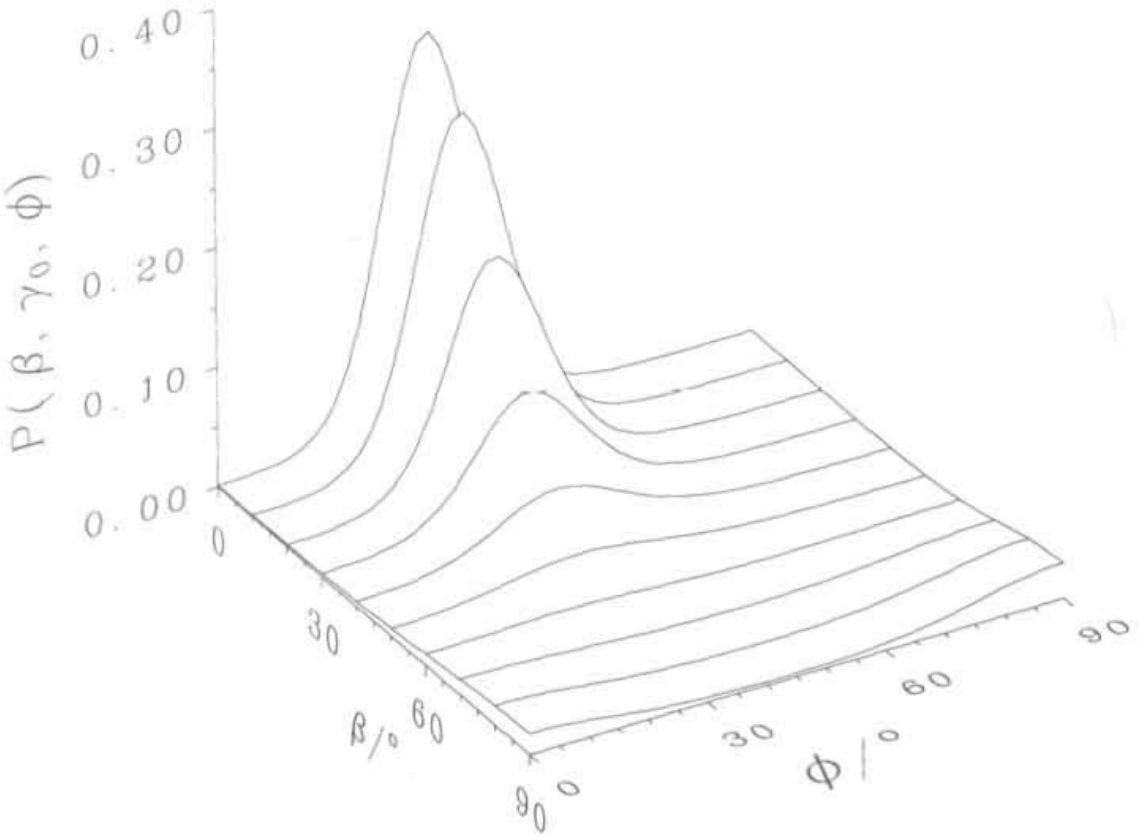

Figure 3: Plot of the orientational–conformational distribution $P(\beta, \gamma_0, \phi)$ with $\gamma_0 = 0°$ for some selected orientations β as obtained from ZLI1132/EBBA data [5] and geometry (a).

sets of experimental couplings in refs. [4, 5] and the resulting coordinates have been averaged to get the following geometry for the $\phi = 0°$ (i.e. $y_i = 0.0$) conformation: $x_1 = 2.16563$, $z_1 = 0.90222$, $x_2 = 2.16753$, $z_2 = 3.38322$, $x_3 = 0.00000$, $z_3 = 4.64063$. The third geometry considered is just that of two perfectly hexagonal phenyl rings with $r_{CH} = 1.081$Å, $r_{CC} = 1.40$Å and all bond angles 120°. The inter–ring distance has been taken as $r_{RR} = 1.52$Å. The results of the MEIO analysis using this latter geometry are very similar to those of geometries (a) and (b) and will not be reported.

We have computed linearly independent combinations t_I of symmetrized couplings T_I using the orthogonalization procedure described above and in ref. [6]. Using a threshold of 10.0Hz (geometry (a)) and 0.5Hz (geometry (b)) for the eigenvalues of the overlap matrix we have found only four linearly independent combinations t_I. In Table 1 we give the percentage contribution of each symmetrized coupling T_I to these orthogonal combinations t_I. The couplings with the highest components are T_1, T_6, T_7 and T_9. The LXNMR experiment determines averages of a set of dipolar couplings or rather of their orthogonalized combinations d_I over the orientational conformational distribution $P(\omega, \phi)$. Thus, according to maximum

entropy [10] the best (least biased) approximation to the true distribution in the uniaxial mesophase obtainable from a LXNMR experiment will be of the form

$$P(\omega, \phi) = \exp[\Lambda(\omega, \phi)]/Z_0, \tag{5}$$

where Z_0 is defined by

$$Z_0 = \int d\omega d\phi \exp[\Lambda(\omega, \phi)]. \tag{6}$$

and where

$$\Lambda(\omega, \phi) = \sum_{I=1}^{n_C} \lambda_I [t_I]^{2,0}_{LAB}(\omega, \phi) \tag{7}$$

plays the role of an effective orientation–conformational potential expanded in the basis functions $[t_I]^{2,0}_{LAB}(\omega, \phi)$. Notice that the functional form of $\Lambda(\omega, \phi)$ is richer than the simple 2 terms Fourier adopted before [4, 5]. From the practical point of view the best set of λ_I is determined minimizing the convex free–energy like functional [11]

$$\Gamma(\{\lambda_I\}) = \ln Z_0 - \sum_{I=1}^{n_C} \lambda_I d_I \tag{8}$$

The maximum entropy analysis of ref. [4] was performed optimizing variational parameters associated to T_1, T_6, T_7 and T_9. It is interesting to notice that the choice of couplings by the authors of ref. [4], based on a physical reasoning, can be automatically obtained using the orthogonalization procedure of ref. [6].

The three sets of dipolar couplings measured in ZLI1132/EBBA, I35 and ZLI1115 have been analyzed with the MEIO method using the two geometries (a) and (b). The four variational parameters associated to the linear combinations t_I were optimized until the minimum of the functional (8) was found. The uncertainties of the MEIO results have been estimated using 50 iterations of the error analysis procedure described in ref. [6] and using a sampling range of $\pm 3\sigma_I$ around the experimental average value of each coupling. The results of our maximum entropy analyses are reported in Table 2 as differences with respect to the experimental couplings. The overall *rms* error σ in Hz and the orientational order parameters S_{xx}, S_{zz} are reported as well. The analyses with geometry (a) give a considerably higher *rms* error than with geometry (b), but this is not surprising since the latter geometry has been previously optimized with respect to the experimental couplings and thus even the orientational order parameters are quite different. Using geometry (b) both couplings T_1 and T_9 are not modulated by ϕ and can be used to completely define the average molecular orientation independently of conformation. On the other hand using geometry (a) all couplings are modulated by ϕ. The molecular geometry plays an important role in the *rms* error σ of the MEIO analysis, but its effects on the resulting conformational distribution function are small. In Figure 2 we report the averaged conformational distribution functions $P(\phi)$ for the three sets of dipolar couplings in ZLI1132/EBBA, I35 and ZLI1115 and geometries (a) and (b). The six

distribution function $P(\phi)$ differ in the position of the most probable conformation less than 2° and have comparable heights. These slight differences are mainly due to the different values of the S_{zz} order parameter in the three solvents. The most probable conformation is $\phi_{max} = 34°$ (geometry (a)) and $\phi_{max} = 35.5°$ (geometry (b)). Furthermore ϕ_{max} does not change with the solvent. We have also separately tested the feasibility for MEIO of finding the maximum at 37° by generating various sets of D_{ij} using a monorotamer distribution peaked at this angle with the same orientational order parameters determined before and using geometries (a), (b). We find by analyzing these data that MEIO can actually return a peak at the correct peak position with an error less than 2°. To examine the importance of rotational–conformational coupling we show in Figure 3 the angle resolved distribution $P(\beta, \gamma, \phi)$, corresponding to the couplings measured in ZLI1115 with geometry (a), at a few selected orientations β and for a fixed angle $\gamma_0 = 0°$. As we see the probability of having a certain conformational angle ϕ is somewhat sensitive to the molecular orientation.

The results of the MEIO analyses show that the "*ad hoc*" fitting of proton coordinates or the use of the so called "*vibrational corrections*" in dipolar couplings [5] do not give any further insight in the structural and conformational study of biphenyl.

In summary, we have analyzed using the MEIO method a new set of high quality data for biphenyl in ZLI1132/EBBA and re–analyzed previous data in ZLI1115 and I35 solvents. We have determined the coupled orientational–conformational distribution showing that the internal distribution changes as the molecule moves from parallel to perpendicular to the director, even if the angle $\phi_{max} = 35 \pm 1°$ remains essentially constant at least for angles between molecule and director up to 60°. We wish to stress that the procedure employed is fully automatic and that the code needed for the analysis is available from the authors.

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