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Calculated NMR chemical shifts of nylon 6: a comparison of the α and γ forms

J. CASANOVAS*
Departament de Química, Escola Universitària Politècnica,
Universitat de Lleida, c/Jaume II, n° 69, Lleida 25001, Spain
E-mail: jcasanovas@quimica.udl.es

C. ALEMÁN*
Departament d'Enginyeria Química, E.T.S. d'Enginyers Industrials de Barcelona,
Universitat Politècnica de Catalunya, Diagonal 647, Barcelona E-08028, Spain
E-mail: carlos.aleman@upc.es

The ^{13}C and ^{15}N chemical shifts of the α and γ crystal forms of nylon 6 have been estimated using *ab initio* calculations (GIAO method) with the B3LYP Density Functional and the 6-311G(d) basis set. Calculations were applied on proper model systems and the agreement with experimental data was quite good in all cases. Comparison between the results obtained for isolated chains and hydrogen bonded sheets allowed to elucidate the influence of the conformation and packing forces in the chemical shifts. These results open up new opportunities for the future use of quantum mechanical calculations as a complementary tool in the determination of the crystal structure of polymers.

1. Introduction

Nylon 6 is an important engineering plastic that has been subject of study from many researches [1–3]. Thus, a large number of papers dealing with its chemical synthesis, structural properties and industrial aspects have been reported during the last five decades. The two latter points are closely related since it was found that physical properties of the nylon 6 fibers depend on its crystalline structure [4, 5]. However, some questions related with the crystalline structure of nylon 6 remain unanswered.

The two most common crystalline structures found in nylon 6 are those named α and γ, the former being thermodynamically the most stable. In both forms the molecular chains are arranged in sheets, which are packed side-by-side, with stabilizing hydrogen bonds running in a single directions. Molecular conformations are however, different; so in the α form the chains are fully extended, whereas in the γ form the methylene next to the amide groups adopts a *skew* conformation, in a way similar to the pleated sheet of proteins. This change produces two distinctive features in the γ form: (i) the repeat unit length is shortened (about 0.35 Å per amide group); and (ii) the amide groups are tilted (about 60°) toward the planes which contain the methylene segment of the chain. Consequently, the hydrogen bonding direction is modified and a monoclinic packing, which is usually described as pseudohexagonal by its peculiar dimensions, is preferred.

The α and γ crystal forms of nylon 6 have been widely investigated and distinguished by X-ray diffraction [6]. Theoretical investigations based on energy calculations and/or simulations of the X-ray diffractions patterns have also been pursued [7]. On the other hand, the crystal structures of nylon 6 have been studied by both ^{13}C and ^{15}N Cross Polarization/Magic Angle Spinning (CP/MAS) NMR spectroscopy [5, 8]. Nevertheless, no theoretical study about the solid-state NMR spectra has been reported until now. In this work we use the GIAO (Gauche Invariant Atomic Orbitals) method to analyze the NMR spectra of the two crystal forms of nylon 6. Thus, shielding properties of the atoms in a magnetic field have been computed by means of *ab initio* quantum mechanical techniques that include electron correlation effects. It should be noted that NMR is a local method insensitive to long range order, but sensitive to both the molecular conformation and the close environment. Results have provided a quantitative and comprehensive understanding of the influence of both intra- and inter-molecular geometric parameters on the computed chemical shifts.

2. Methods

2.1. Molecular models

There is a substantial confusion regarding the crystalline structures of nylon 6 since different unit cells have been reported for both the α and γ forms [9]. However, this variability was explained by Parker and

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*Authors to whom all correspondence should be addressed.

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Lindenmeyer by slight crystal structural changes depending on the annealing conditions [10]. In this work we used the unit cell deduced by Holmes *et al.* for the α form: $a = 9.56$ Å, b (fiber axis) $= 17.24$ Å, $c = 8.01$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 67.5^\circ$ [6]. This unit cell contains four molecules, which adopt an all-*trans* conformation, distributed in two hydrogen bonded sheets (Fig. 1a). It is worth noting that polymer chains are arranged in antiparallel within the sheets.

The structure reported by Arimoto [6] has been used for describing the γ form. This consists of two molecules packed in antiparallel within a unit cell of dimensions $a = 9.33$ Å, b (fiber axis) $= 16.88$ Å, $c = 4.78$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 121^\circ$. In this case the chain axis is shorter than for the α form, since the two dihedral angles adjacent to the amide groups have significantly smaller values, *i.e.*, about ±120° (Fig. 1b). In contrast to the α form, hydrogen bonds are established between sheets.

Molecular systems were built by replacing the polymer chains at crystal structures described for the α and γ forms by small model molecules (see below). The standard bond lengths and bond angles for polyamides were considered.

2.2. GIAO calculations of chemical shifts

In quantum mechanical terms, the shielding constant σ is the mixed second-order perturbation of the energy expectation value of the molecule with respect to the exterior magnetic field B and the nuclear magnetic moment μ of the nucleous M in question [11].

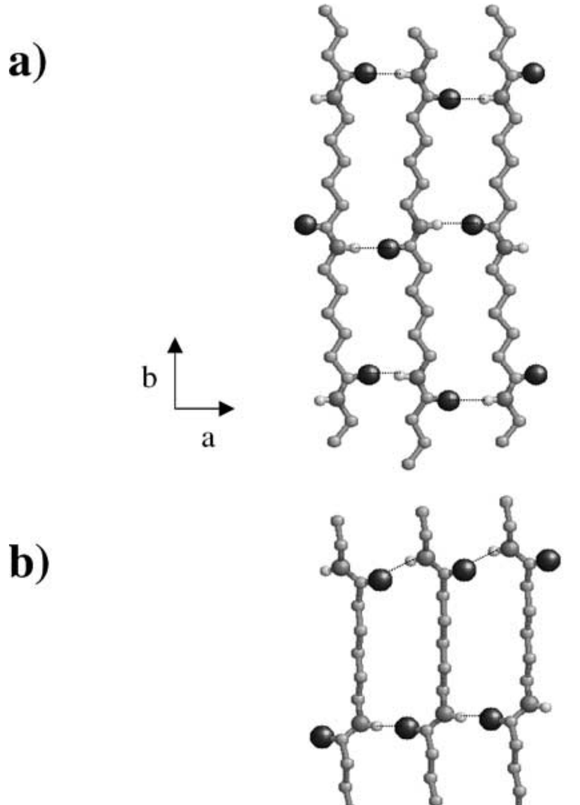


Figure 1 Atomic scheme displaying three hydrogen bonded chains in the α (a) and γ (b) form of nylon 6. It should be noted that in the α form the conformation is all-*trans* while in the γ form the planes containing the amide and methylene groups are tilted by about 60°.

$$\sigma^M_{\alpha\beta} = \frac{\partial^2 E}{\partial \mu^M_\alpha \partial B_\beta} \qquad \alpha, \beta = x, y, z \qquad (1)$$

where $E = \langle H \rangle$ and H is the full Hamiltonian of the system including magnetic perturbations. For powder samples, MAS-NMR experiments only detect the isotropic part of the tensor, σ_{iso}. Thus, in this case all orientations of the chemical shift tensor relative to the external magnetic field occur.

$$\sigma_{\text{iso}} = \frac{\sigma_{\text{xx}} + \sigma_{\text{yy}} + \sigma_{\text{zz}}}{3} \qquad (2)$$

Both carbon and nitrogen isotropic shielding constants, $\sigma(^{13}\text{C})$ and $\sigma(^{15}\text{N})$, of nylon 6 were computed using perturbation theory and the GIAO method [12] implemented in the Gaussian 94 program package [13]. It should be emphasized that GIAO calculations are very expensive from a computational point of view and, therefore, they are usually applied to small model systems.

The electronic structure of the molecular models was determined using Density Functional Theory (DFT) methods, which include some electron correlation effects not present at the Hartree-Fock level. More specifically, the Becke's [14] three-parameter hybrid functional with gradient corrections provided by the LYP functional [15] (B3LYP) was used. The Kohn-Sham orbitals were constructed using Gaussian-type atomic orbitals basis sets. All the calculations were performed using the 6-311G(d) basis set [16] to describe the C, H and O atoms of the models under study.

Theoretical calculations yield absolute values with respect to the bare nucleous *in vacuo* whereas experimental data refer to a references (TMS and NH_3 for ^{13}C and ^{15}N, respectively). Thus, the experimental scale δ (chemical shift) is related to the theoretical scale σ *via*

$$\delta = \sigma - \sigma_0 \qquad (3)$$

where σ_0 is the theoretical value of the reference. The ^{13}C isotropic shielding constant in TMS, $\sigma(^{13}\text{C})_{\text{TMS}} = 184.2$ ppm, was computed in a previous work at the level of theory described above [17]. The ^{15}N shielding constant in NH_3, $\sigma(^{15}\text{N})_{\text{NH}_3} = 269.9$ ppm, has been computed in the same way for the present study.

2.3. Comparison with experiment

The NMR chemical shifts for the α and γ crystalline forms of nylon 6 have been compared by different authors in the last decade. Hatfield *et al.* [8] characterized these two phases by solid state ^{13}C and ^{15}N NMR. The results achieved by these authors present important discrepancies in some carbon atoms with respect to those reported by Weeding *et al.* [8] two years before. Table I compares the chemical shifts provided in such two studies. In a very recent work, Schreiber *et al.* [5] re-investigated the α and γ forms of nylon 6 using ^{13}C solid state spectroscopy. As can be seen in Table I the results were very similar to those published by Hatfield

TABLE I Comparison among the experimental chemical shifts (δ; in ppm) of ^{13}C and ^{15}N atoms reported by different authors for the α and γ crystal forms of nylon 6. Differences between the values of the two forms ($\Delta\delta$; in ppm) are also displayed

Form	C1	C2	C3	C4	C5	C6	N	Ref
$\alpha(\delta)$	173.4	36.7	26.5	30.4	30.4	43.6	116.5	[8]
$\gamma(\delta)$	173.0	37.8	30.1	30.1	34.1	39.9	121.8	[8]
$lpha - \gamma(\Delta\delta)$	0.4	−1.1	−3.6	0.3	−3.7	3.7	−5.3	
$lpha(\delta)$	173.4	37.8	26.5	30.1	30.1	42.8	–	[8]
$\gamma(\delta)$	173.4	33.9	26.7	30.0	30.0	39.9	–	[8]
$lpha - \gamma(\Delta\delta)$	0.0	3.9	−0.2	0.1	0.1	2.9		
$lpha(\delta)$	–	36.5	26.2	30.2	30.2	43.2	–	[5]
$\gamma(\delta)$	–	37.5	30.2	30.2	33.9	39.9	–	[5]
$lpha - \gamma(\Delta\delta)$		−1.0	−4.0	0.0	−3.7	3.3		

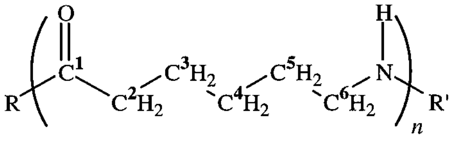
et al. Moreover, ^{13}C MAS spectra were used to determine the relative amount of α and γ forms in a sample, the results being in good agreement with wide-angle X-ray spectroscopy results. According to these features, the chemical shifts reported by Hatfield *et al.* [8] and Schreiber *et al.* [5] were used to compare with our quantum mechanical results.

3. Results

Results have been divided in two different sections. First, we have compared the chemical shifts predicted for the fully-extended and semi-extended conformations distinctive of the α and γ forms, respectively. Thus, the changes properly induced by the tilting of the amide planes with respect to the aliphatic segment will be characterized. After this, the influence of the packing interactions has been analyzed by comparing the results achieved from the calculations of two and three interacting chains.

3.1. Molecular conformation

Three model compounds, denoted **I**, **II** and **III**, were considered to mimic a molecular chain of nylon 6 in the α and γ crystal forms. These consisted of:



I: *n*=1; R= CH_3-NH; R'= CO-CH_3

II: *n*=1; R= CH_3-CH_2-CH_2-NH; R'= CO-CH_2-CH_2-CH_3

III: **I**: *n*=2; R= CH_3-NH; R'= CO-CH_3

For the α form all the torsional angles of the model compounds were kept at 180°, while for the γ form the amide groups were rotated by 60° relative to the plane of the methylene chain. The $\delta(^{13}C)$ and $\delta(^{15}N)$ values computed for the atoms located at the central part of **I**, **II** and **III** are displayed in Table II. It is worth noting that the chemical shifts predicted for such three model compounds are very similar indicating that the simplest one, **I**, is enough to provide a good description of the molecular chain.

On the other hand, results listed in Table II reveals that the computed chemical shifts are quite sensible to the conformational difference between the α and γ forms. This is reflected in the $\Delta\delta(\alpha - \gamma)$ values, which correspond to the difference between the chemical shifts computed for the α and γ conformations. Comparison between the theoretical and experimental $\Delta\delta(\alpha - \gamma)$ values indicates a satisfactory agreement for C1, C2, C3, C5 and C6 atoms. Thus, for such atoms the sign of $\Delta\delta(\alpha - \gamma)$ is correctly reproduced. Moreover, for all the atoms with exception of C2 the difference is lower than 1.5 ppm, for such atom being 3.3 ppm. A detailed comparison between the results displayed in Tables I and II shows that the source of error in C2 arises from the poor reproduction of the chemical shift in the γ form. Thus, the $\delta(^{13}C_2)$ computed for the γ form is overestimated by 4.1 ppm with respect to the experimental value.

TABLE II Theoretical chemical shifts (δ; in ppm) of ^{13}C and ^{15}N atoms for the model compounds **I**, **II** and **III** (see text). The values listed correspond to those obtained for the conformations characteristic of the α and γ forms. Differences between the values of the two forms ($\Delta\delta$; in ppm) are also displayed for each compound

No.	Form	C1	C2	C3	C4	C5	C6	N
I	$\alpha(\delta)$	171.8	37.5	30.1	31.9	33.8	43.9	131.0
	$\gamma(\delta)$	170.1	41.9	32.2	32.9	37.2	41.1	143.0
	$\alpha - \gamma(\Delta\delta)$	1.7	−4.4	−2.1	−1.0	−3.4	2.8	−12.0
II	$\alpha(\delta)$	171.4	37.7	30.1	32.0	33.8	43.8	133.1
	$\gamma(\delta)$	169.4	42.0	32.2	33.0	37.2	40.8	141.2
	$\alpha - \gamma(\Delta\delta)$	2.0	−4.3	−2.1	−1.0	−3.4	3.0	−8.1
III	$\alpha(\delta)$	171.4	37.5	30.1	31.9	33.7	43.8	133.6
	$\gamma(\delta)$	169.6	41.9	32.1	32.9	37.1	40.8	141.7
	$\alpha - \gamma(\Delta\delta)$	1.8	−4.4	−2.0	−1.0	−3.4	3.0	−8.1

It is worth noting that the chemical shifts measured for these atoms are substantially different in the α and γ forms. The results achieved for the isolated molecule reveal that such differences are not induced by intermolecular crystal forces but they are consequence of the rotation of the amide plane in the γ form.

Table III shows the Mullinken partial atomic charges obtained for the model compound **I**. It is worth noting that an electron density transfer towards the C1 atom is induced in the γ form by the amide rotation. The electron transfer produces a deshielding of C3 and a shielding of C1. This electronic effect, which may be attributed to the overlap between the C2—C3 bond and the π orbital of the C=O moiety, as was previously suggested by Hatfield *et al.* [8], produces a deshielding of C3 (2.1 ppm) and a shielding of C1 (1.7 ppm). On the other hand, the atomic charge density of C5 also decreases by the rotation of the amide group inducing a deshielding of such carbon atom (3.4 ppm).

The results obtained for C4 reveal an inversion in the sign of $\Delta\delta(\alpha - \gamma)$ when a single molecule is considered in the calculations (Table II). However, the difference with respect to the experimental value is only of 1.3 ppm indicating a reasonably description of this carbon atom.

On the other hand, a qualitative agreement between the experimental and theoretical $\Delta\delta(\alpha - \gamma)$ values was obtained for the N atom as reveals the negative sign of such parameter. However, the error in this case was of almost 7 ppm and the $\delta(^{15}N)$ values of the α and γ forms were overestimated by 23.5 and 21.2 ppm, respectively. This failure suggests that the ^{15}N NMR chemical shifts in nylon 6 may be largely influence by hydrogen bonding interactions.

TABLE III Partial atomic charges (in units of electron) for the molecular conformations characteristic of the α and γ forms of nylon 6. Charges were computed using the model compund **I** (see text)

No.	C1	O	C2	C3	C4	C5	C6	N	H(N)
α	0.503	−0.384	−0.104	0.041	0.000	−0.051	0.250	−0.565	0.339
γ	0.481	−0.396	−0.080	0.035	−0.002	0.003	0.188	−0.558	0.337

3.2. Hydrogen bonded chains

Once the influence of the molecular conformation in the NMR spectra of crystalline nylon 6 was determined, our next step was to investigate the hydrogen bonding effects. These were considered through the supermolecule approach by including explicitly some neighboring molecules. It should be noted that the computational cost of GIAO calculations is very high, being completely prohibitive for complexes constituted by more than two interacting model molecules. Thus, pilot calculations (data not shown) were performed in order to find a reduced model able to provide a suitable description of the system. It was found that the complex constituted by two interacting chains, each one described by the model compound **I**, provides almost the same results that a reduced complex in which one chain is replaced by two formamide molecules located at the hydrogen bonding positions. Thus, the largest and average shielding constant differences between these complexes were 0.7 and 0.3 ppm, respectively. According to this, chemical shifts were computed for the α and γ forms of nylon 6 considering a complex constituted by a chain described by **I** and four formamide molecules arranged at all the hydrogen bonding positions. These complexes, which are displayed in Fig. 2, simulate the interactions among three chains and were used to describe the hydrogen bonding sheets of the α and γ forms.

NMR chemical shifts are listed in Table IV. The absolute chemical shifts predicted for carbon atoms are well reproduced for both the α and γ forms, as is demonstrated by the large Pearson correlation coefficient ($r > 0.95$) and the scaling coefficient close to one ($1.00 < c < 1.06$) obtained for the fittings $y = cx$. Furthermore, a good agreement between the theoretical and experimental $\Delta\delta(\alpha-\gamma)$ values was obtained for the C2, C3, C5 and C6 atoms. More specifically, the values computed for C2, C5 and C6 are very similar to those reported by Hatfield *et al.* [8] and Schreiber *et al.* [5], while $\Delta\delta(\alpha-\gamma)$ is overestimated by −1.9 ppm for C3. On the other hand, the $\Delta\delta(\alpha-\gamma)$ predicted for the C1 atom was −1.6 ppm, the observed value being 0.4 ppm reported by Hatfield *et al.* [8]. This discrepancy is probably due to the simplicity of our molecular model. Thus, the amide carbon is expected to be particularly sensitive to the surrounding environment.

TABLE IV Chemical shifts (δ; in ppm) of ^{13}C and ^{15}N atoms for the α and γ forms of nylon 6 computed using the complexes displayed in Fig. 2. Differences between the values of the two forms ($\Delta\delta$; in ppm) are also displayed for each complex

Form	C1	C2	C3	C4	C5	C6	N
$\alpha(\delta)$	171.8	38.4	30.1	32.4	33.1	44.3	141.0
$\gamma(\delta)$	173.4	38.6	31.8	33.5	36.9	40.3	135.4
$\alpha-\gamma(\Delta\delta)$	−1.6	−0.2	−1.7	−1.0	−3.8	4.0	5.6

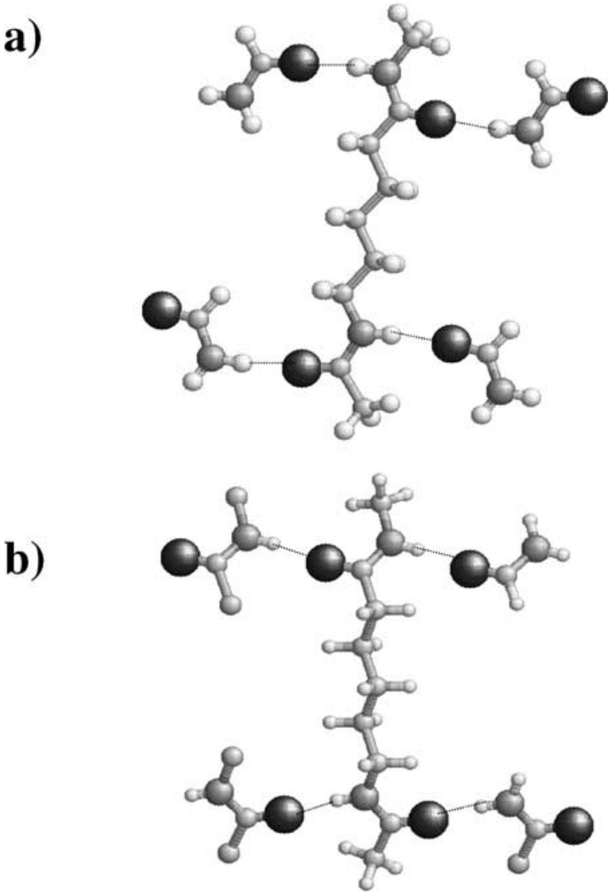


Figure 2 Atomic scheme displaying the complexes used to compute the chemical shifts of the α (a) and γ (b) forms of nylon 6.

It should be noted that the influence of the intermolecular hydrogen bonds is very remarkable for C2. Thus, the $\Delta\delta(\alpha-\gamma)$ values predicted for such carbon atom are −4.4 and −0.2 ppm in absence and presence of such forces, respectively, the latter being in better agreement with the experimental value. Moreover, comparison between the results displayed in Tables II and IV indicates that C1 is also very sensible to enviromental effects. Thus, the $\Delta\delta(\alpha-\gamma)$ value predicted for this atom change from 1.7 to −1.6 ppm when hydrogen bonding interactions are taken into account, the experimental value being 0.4 ppm. These results suggest that van der Waals interactions between adjacent sheets could also induce significant changes.

The $\delta(^{15}\mathrm{N})$ values computed for the two complexes displayed in Fig. 2 are in poor agreement with experimental data. The relative order of the absolute chemical shifts predicted for the α and γ forms is inverted with respect to that experimentally detected. Furthermore, the values are overestimated by 24.5 and 13.6 ppm for the α and γ forms, respectively. However, it is interesting to note that $\Delta\delta(\alpha-\gamma)$ computed for the hydrogen bonded sheets is closer to the experimental data than that derived from the isolated model molecules.

4. Discussion

In this study we analyze the ^{13}C and ^{15}N NMR chemical shifts of the α and γ crystal forms of nylon 6 using first principle calculations. First, calculations were performed on a model molecule enoughly large to mimic an isolated chain of nylon 6. A remarkable agreement between experiment and theory was obtained for the carbon atoms when the extended and pleated conformations characteristic of the α and γ forms were considered. It should be mentioned that the chemical shift is a local property with only a limited number of atomic interactions governing shielding. Thus, for some atoms such interactions are mainly associated to the molecular conformation, the description of the crystal packing being not needed to reproduce their shifts.

The simplest method for evaluating the effects of the surrounding molecules in a crystal structure is the supermolecule approach, where some neighboring molecules are explicitly considered. However, because of the large number of atoms involved, calculations of a complex constituted by three interacting chains of nylon 6 are excessively expensive from a computational point of view, even on the IBM-SP2 computer we have used. Thus, in order to design a simple complex able to collect the essential trends of the crystal packing, we made two assumptions. First, the influence of the hydrogen bonds in the chemical shifts is larger than the effect of the van der Waals interactions and therefore, the stacking of the hydrogen bonded sheets can be neglected in the calculations. Second, the crystalline environment within a hydrogen bonded sheet can be simulated by surrounding with formamide molecules the amide groups of the nylon 6 chain. It should be mentioned that this way of simulating the crystal environment was successfully used by us for studying the conformational preferences of polyglycine [18]. According to these assumptions the ^{13}C and ^{15}N NMR chemical shifts of the α and γ crystal forms were computed using a complex constituted by a chain of nylon 6 surrounded by four formamide molecules, which were placed at the hydrogen bonded positions.

Overall, the agreement between the observed and computed chemical shifts is satisfactory for the carbon atoms. Thus, the unsigned average difference between the experimental and theoretical values was 1.1 and 1.8 ppm for $\Delta\delta(\alpha - \gamma)$ and $\delta(^{13}C)$, respectively. So the complex used to mimic the crystal structures of nylon 6 is able to capture the essential trends of both the α and γ forms. Moreover, comparison of the results obtained for a single chain and for the complex allows explain for each crystal form the role of packing forces on the observed chemical shifts.

Regarding to the nitrogen atom, the chemical shifts predicted for the α and γ forms are overestimated by 24.5 and 13.6 ppm, respectively, with respect to the experimental values. This poor result can be attributed to several sources of errors. First, the level of theory used to describe the system under study. The electron correlation largely affects the NMR parameters. This is partially included at the B3LYP level but better results can be obtained with more sophisticated methods [19]. With respect to the basis size, theoretical chemical shifts of good quality are obtained by using large basis sets [19]. However, the 6-311G(d,) basis set has provided reliable results [20, 21]. Moreover, the ^{15}N shielding constant calculated for the NH_3 (269.9 ppm), which is the solvent used as reference, is in good agreement with the experimental value (264.5 ppm) [22]. Furthermore, calculations using other quantum mechanical methods and larger basis sets (data not shown) do not provide any substantial change in the ^{15}N chemical shift. The second source of error is the size of the complex used to describe the α and γ forms of nylon 6. Thus, hydrogen bonds within the sheet were the only interaction included in the calculations, the van der Waals interactions between adjacent sheets being completely neglected. Although consideration of larger complexes is very desirable, it is not feasible from a computational point of view.

In summary, in spite of the limitations of the model systems under study, the theoretical strategy we have used is able to distinguish between the α and γ crystal forms of nylon 6. Accordingly, GIAO calculations in combination with experimental NMR provide a way to have a thorough look on the local organization of crystallized polymeric systems. They can be a useful complement of diffraction methods, which are usually combined with energy calculations, to determine the crystal structure of polymers.

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