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Conformations of Nylons 1,*n* According to the Number of Methylene Carbons

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ABSTRACT: We analyze the conformation of several members of the nylon 1,*n* family with the linked-atom least-squares (LALS) methodology applied to X-ray and electron diffraction data and with quantum mechanical calculations. We concluded that new structures, characterized by a particular conformation of the isolated methylene unit between NH groups, are possible in this family of nylons. Close amide groups are oriented in opposite directions. Different conformations depending on the polymethylene segments between the carbonyl groups are also found and energetically studied according to the number of methylene carbons. In the case of an odd and low *n* value, a 3-fold helical conformation responsible for three hydrogen bond directions seems to be stabilized. On the other hand, polymers with an even *n* value are characterized by a 2/*b* symmetry and therefore a single hydrogen bond direction. This is the first time that these types of structures have been observed in aliphatic polyamides.

Introduction

Aliphatic polyamides (nylons) are an interesting group of polymers with important industrial uses, which are closely related to proteins.[1,2] Both polyamides and proteins present NH...O=C hydrogen bonds, which play a key role in determining their structural characteristics. Thus, although aliphatic polyamides lack the amino acid side chains, they exhibit some structural features found in fibrous proteins. However, only two basic crystalline structures, named the α[3] and γ[4] forms, are found in nylons, whereas proteins present a major structural variability. In both forms the molecular chains are organized in parallel sheets, with the stabilizing hydrogen bonds running in a single direction. Molecular conformations are however different, so in the α form the chains are fully extended, whereas in the γ form the methylenes next to the amide groups are in a skew conformation, in a way similar to pleated sheets in 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 segments of the chain. Consequently, the hydrogen bond direction is modified and a pseudohexagonal packing is preferred.

In recent years, our laboratory has carried out a systematic effort aimed to investigate nylons with structures different from the conventional ones, characterized by more than one hydrogen bond direction.[5-15] All the polymers investigated have a common structural feature: they have amide groups very close in space; thus, their strong interactions may favor different conformations. In this way we found that polymers with ...–$CONHCH_2CONH$–... and ...$NHCOCH_2CONH$–... groups have structures with three[5-10] and two[11,12] hydrogen bond directions, respectively, independent of the number of methylenes between them. At the present time we are interested in the conformations of polymers which have similar groups: nylons 1,*n*. These are molecules with a straight polymethylene segment and no branches:

$$\ldots\text{–}\mathbf{CONHCH_2NHCO}(CH_2)_{n-2}\text{–}\ldots$$

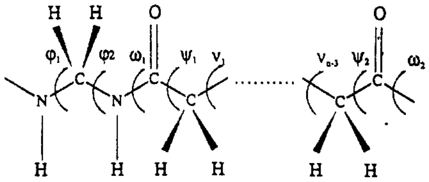

Figure 1. Representation of a general nylon 1,*n* repeat unit backbone showing the definition of torsional angles as used in Table 1.

Several members of this family of nylons have been investigated by means of X-ray and electron diffraction.[6,12-15] These data show that two structures are possible according to the *n* values. Polymers with low and odd *n* give crystals with doughnutlike ($n = 3$)[6] or rounded ($n = 5$)[15] morphologies. Their diffraction data can be indexed on the basis of hexagonal lattices and their *hk*0 electron diffraction patterns exhibit a 6/*mmm* symmetry. All the other studied polymers ($n = 4$,[13] $n = 6, 8, 10$,[14] $n = 12$[15]) give elongated crystals, *h*0*l* electron diffraction patterns with 2/*mmm* symmetry, and diffraction data indexed as a monoclinic unit cell. In all cases however, the repeat unit length is shorter than expected for a fully extended conformation.

In this work we address a study of the conformational preferences of nylons 1,*n*. For this purpose two different and well-established methodologies were used. First, we investigated the crystalline structure of several members of this family of nylons, taking into account X-ray and electron diffraction data, packing, and geometric restrictions using the linked-atom least-squares (LALS) methodology.[16] However, since the LALS methodology is rather crude from an energetic point of view, we carried out more detailed energy calculations. Thus, second, we carried out an energy analysis of all the molecular conformations derived from experimental data using semiempirical and ab initio SCF–MO quantum mechanical methods.

Methods

Structural Modeling. Experimental data for nylons 1,5 and 1,6 were used to study the chain conformation. The results were satisfactorily extrapolated to the remaining polymers. The description of one generic residue of nylon 1,*n* is shown in Figure 1. Approximate models with a sound stereochemistry were built and then refined using the LALS methodology.[16] Standard bond lengths and angles for polyamides were adopted to build the

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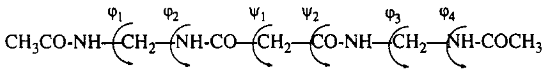

$CH_3CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}CO\text{-}CH_2\text{-}CO\text{-}NH\text{-}CH_2\text{-}NH\text{-}COCH_3$

(II) $CH_3CO\text{-}NHCH_2NH\text{-}COCH_2CH_2CO\text{-}NHCH_2NH\text{-}COCH_3$

(III) $CH_3CO\text{-}NHCH_2NH\text{-}COCH_2CH_2CH_2CO\text{-}NHCH_2NH\text{-}COCH_3$

(IV) $CH_3CO\text{-}NHCH_2NH\text{-}COCH_2CH_2CH_2CH_2CO\text{-}NHCH_2NH\text{-}COCH_3$

(V) $CH_3CO\text{-}NHCH_2NH\text{-}COCH_2CH_2CH_2CH_2CH_2CO\text{-}NHCH_2NH\text{-}COCH_3$

Figure 2. Model molecules selected for quantum mechanical calculations: (I) nylon 1,3; (II) nylon 1,4; (III) nylon 1,5; (IV) nylon 1,6; (V) nylon 1,7. The torsional angles that define the conformation of the model molecules are the φ_1, φ_2, ψ_1, ψ_2, φ_3, and φ_4 shown specifically for I.

repeating unit and were held fixed throughout the whole modeling process. The torsional angles ω_i and ν_i were kept in the trans conformation for all the models investigated. Consequently, only the torsional angles next to the amide groups (φ_i and ψ_i) and the positional parameters fixing the chain in the unit cell were needed to define the chain conformation and the packing analysis. The models were refined according to the experimental chain repeat length (8.7 and 10.1 Å for nylons 1,5 and 1,6, respectively), the packing constraints due to the unit cell dimensions, and the optimum hydrogen bond geometry. Diffraction data were also used to test and improve the quality of the models. Calculated structure factors were corrected by an isotropic temperature factor (B = 5 Å^2).

Energy Calculations. Another way to discriminate between the stereochemically satisfactory models is by a conformational energy criteria. Thus, the structural features found from the LALS analysis were studied using semiempirical and ab initio SCF–MO quantum mechanical calculations. The Austin Model 1 (AM1) method[17] was selected for semiempirical calculations. This is a well-known method which provides molecular geometries very similar to those found by ab initio calculations.[17–21] Nevertheless, it uses minimal basis sets consisting of Slater type orbitals (STO), and therefore more sophisticated calculations are required for a quantitative conformational analysis. Thus, the reliability of the AM1 method in describing the conformational behavior of the nylons 1,n was ensured by comparison with ab initio calculations using the 4-31G[22] basis set.

Figure 2 shows the model molecules selected to mimic the different members of the nylon 1,n family. Their conformational angles are defined following the same nomenclature used in Figure 1. Geometry optimizations, with all backbone torsional angles fixed at their LALS values, were carried out using the AM1 method.

A contour map of the conformational energy as a function of the dihedral angles φ and ψ was generated for the model molecule of nylon 1,3 using the AM1 method. The potential energy surface was evaluated using a grid of 30° and considering the same relationships of torsional angles used in the LALS calculations. Thus, the following symmetry constraints were applied: $\varphi_1 = \varphi_2 = \varphi_3 = \varphi_4$ and $\psi_1 = \psi_2$ (see Figure 2). Torsional angles ω_i and ν_i were held fixed at 180°, while all other geometrical parameters were relaxed.

Ab initio calculations were performed with the HONDO 7.0 program.[23] Semiempirical calculations were performed with a locally modified version[24] of the MOPAC program,[25] using the standard AM1 parameters.[17] Calculations were performed on an IBM 3090/600 at the "CEntre de Supercomputació de CAtalunya" (CESCA).

Results

Two models appear as the most feasible for nylon 1,6, in particular, and for polymers with an even n value in general. The first model consists of a pseudohexagonal packing of 2_1 helices with mirror planes perpendicular to the chain direction through every isolated methylene group. It is like a conventional γ form, although the refined torsional angles (±108°) are slightly different from those reported for other nylons (±120° to ±140°). Indeed, the experimental chain repeat length (10.1 Å) is slightly shorter than expected by extrapolation from the values found in other nylons with a γ structure 10.3–10.4 Å.[4] The second model is based on a particular conformation of the isolated methylene group ($\varphi_1 = \varphi_2 \approx 87°$) as has been observed[26] and calculated[19] in some methylene diamides. In this conformation the close amide groups are oriented in opposite directions, whereas in the γ form they are oriented in a unfavorable parallel orientation (Figure 3a,b). Molecular chains have a center of symmetry in the middle of the ...–$(CH_2)_4$–... methylene segment and a binary axis perpendicular to the chain direction through isolated methylene groups, which maintain the adirectional configuration of the polymer. This symmetry causes equivalent torsional angles in consecutive repeat units to be equal but with inverted sign.

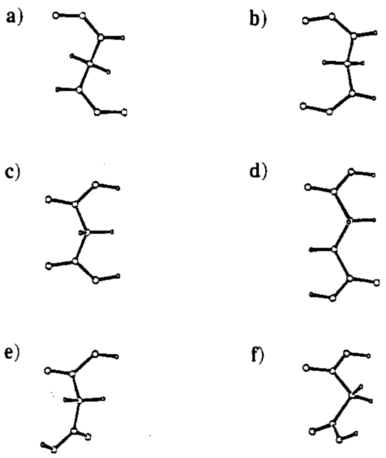

Figure 3. Antiparallel (a) and parallel (b) orientation for two amide groups separated by a unique methylene group according to the proposed structure and to the γ form. Carbonyls separated by an odd or an even number of methylene groups are placed in parallel (c) or antiparallel (d) orientation, respectively, when the methylene segments have a typical γ conformation. Amide groups make an angle of 120° (e) or 60° (f) when the torsional angles take respectively the values $\psi_1 = \psi_2 \approx -120°$ and $\psi_1 = \psi_2 \approx -150°$.

Table 1 presents compared data for the two models. Both have a single hydrogen bond direction (Figure 4) with a satisfactory geometry and without significative contacts. R factors ($\sum|F_o - F_c|/\sum F_o$) favor model II. However, due to the poor pattern quality and the limited number of reflections used in the calculations, the differences are not determinant. The $2/mmm$ symmetry of the electron diffraction pattern also points to model II, since a $2/m$ symmetry is expected for model I.

Table 2 shows the relative energies of both models computed at the AM1 and ab initio 4-31G levels for model molecules of nylons 1,4 and 1,6. Results agree with LALS calculations independently of the computational procedure, model I being less stable than model II by around 9 and 15 kcal/mol at the semiempirical and ab initio levels, respectively. This must be attributed to the electrostatic interactions between the neighbor amide groups. Thus, for model I they are repulsive due to the parallel orientation of the amide groups, whereas for the model II they are attractive. Furthermore, within each computational procedure a similar energetic difference between models I and II was obtained independently of the number of methylene units. On the other hand, energy values suggest that the AM1 potential energy surfaces are flat with respect to the 4-31G ones, in good agreement with previous conformational studies of polyamides.[27] AM1 computed dipole moments were also included in the table. As can

Table 1. Conformational Parameters, Hydrogen Bond Geometry, and *R* Factors for Different Models of Nylons 1,6 and 1,5

	nylon 1,6		nylon 1,5	
	model I	model II	model III	model IV
mol sym	$2_1/m$	$2/b$	3_22	6_522
space group	$P2_1/m$	$B2/b11$	$P3_212$	$P6_522$
cell param				
a (Å)	4.68	8.04	4.79	4.79
b (Å)	20.20[a]	20.20[a]	4.79	4.79
c (Å)	4.79	4.79	26.10[b]	52.20[b]
α	90	90	90	90
β	120.8	90	90	90
γ	90	90	120	120
torsional angle				
φ_1	−107.7	+87.5	+88.0	+87.1
φ_2	+107.7	+87.5	+88.0	+87.1
ψ_1	−107.7	−120.0	−157.4	−119.9
ψ_2	+107.7	+120.0	−157.4	−119.9
ω_1	180.0	180.0	180.0	180.0
ω_2	180.0	180.0	180.0	180.0
H bond geometry				
d(H...O) (Å)	1.72	1.87	1.86	1.64
d(N...O) (Å)	2.72	2.82	2.82	2.62
∠NHO (deg)	177.0	158.0	159.0	164.0
R factor				
X-ray diffraction data (%)	20.2	14.1	21.2	47.4
electron diffraction data (%)	19.4	14.4	18.8	33.9

[a] Fiber identity period for monoclinic lattices. [b] Fiber identity period for hexagonal lattices.

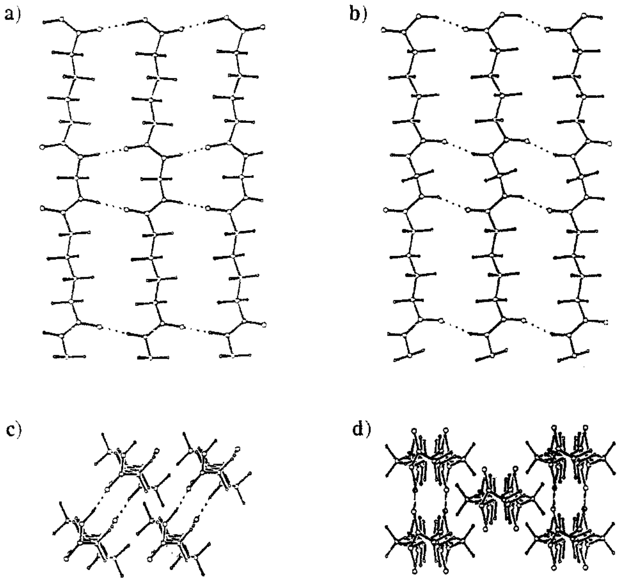

Figure 4. Hydrogen bonding between three neighboring chains of nylon 1,6 according to models I (a) and II (b). Drawings (c) and (d) correspond to the equatorial projections of the unit cell for models I and II, respectively. A centered unit cell with a space group $B2/b11$ is necessary in order to keep the resultant molecular symmetry.

be seen both models keep the apolar configuration of the polymer.

Two models also appear possible for nylon 1,5 and extensively for nylon 1,3. They are characterized by three hydrogen bond directions according to the 6/*mmm* symmetry of the electron diffraction patterns. So, we have generated helical structures with a 3-fold or a 6-fold screw axis. The torsional angles of the methylene diamide unit were kept fixed close to their low energy values ($\varphi_1 = \varphi_2 = 80 \pm 10°$).[19] Basically, only the conformation of the methylene segment between the carbonyl groups has been changed with respect to the models referred to above.

Table 2. Calculated Energies and Dipole Moments for the Different Monoclinic Models of Nylons 1,4 and 1,6[a]

	nylon 1,4		nylon 1,6	
	model I	model II	model I	model II
ΔE_{AM1}	8.5	0.0	8.9	0.0
$\Delta E_{4\text{-}31G}$	14.7	0.0	15.4	0.0
μ_{AM1}	0.0	0.0	0.0	0.0

[a] The model molecules studied correspond to those indicated in Figure 2. ΔE_{AM1} and $\Delta E_{4\text{-}31G}$ refer to the relative energies (in kcal/mol) computed at the semiempirical AM1 and ab initio 4-31G levels, respectively. μ_{AM1} refers to the dipole moment (in D) at the semiempirical AM1 level. The molecular geometries were calculated by optimizing bond lengths and angles using the AM1 method, whereas the torsional angles were kept fixed in the values provided by the LALS refinements (see Table 1).

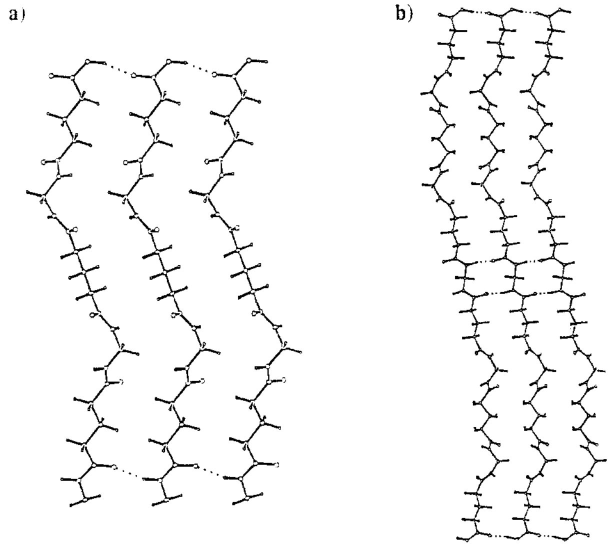

Figure 5. Side view of three neighboring molecules of nylon 1,5: (a) model III; (b) model IV.

Indeed, carbonyl groups separated by an odd number of methylene groups would be placed in an unfavorable parallel orientation when the conformation is $\psi_1 = -\psi_2$. This is not the situation for nylons 1,*n*=even (Figure 3c,d) and will not be important for long methylene segments. Conformations with $\psi_1 = \psi_2 = -120°$ (or 120°) and $\psi_1 = \psi_2 = -155°$ (or +155°) produce rotations of 120° and 60°, respectively, between the C–O directions (Figure 3e,f), which justify the required helical symmetry. Furthermore, malonamide derivatives, used as reference structures, show a characteristic conformation with both ψ angles in the 100–150° range.[28-30]

The proposed models, III and IV, correspond to a hexagonal packing of 3_2 and 6_5 helices, respectively. As there are not asymmetrical carbon atoms, 3_1 and 6_1 helices are equally probable and correspond to conformations with all equivalent torsional angles' signs inverted. However, in order to place correctly all the hydrogen bonds, only helices with the same handedness can be present within a given crystallite. Molecular symmetries are also characterized by binary axes perpendicular to the fold axis that preserve the molecular adirectionality. Results are displayed in Table 1. Both models were found without significative contacts and, therefore, appear stereochemically acceptable. All hydrogen bonds are allowed to be formed with length and angle values within the standard ranges. Molecular drawings of chains built according to the models are given in Figures 5 and 6. In this case the models have not been refined against X-ray data due to the poor quality of the available diagrams and only a qualitative evaluation of diagrams has been taken into

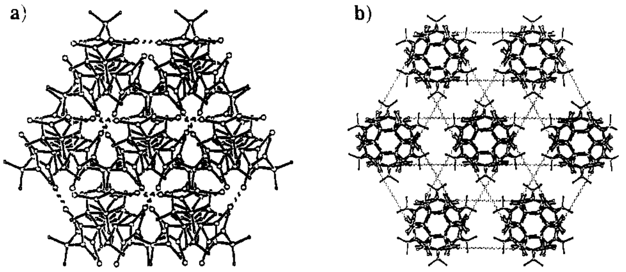

Figure 6. Equatorial projections of a centered molecule and its six surrounding neighbors for nylon 1,5: (a) model III; (b) model IV. In the last case molecular chains have been drawn with an increased separation between them in order to show hydrogen bonds (dashed lines) more clearly.

Table 3. Calculated Energies and Dipole Moments for the Different Hexagonal Models of Nylons 1,3 and 1,5[a]

	nylon 1,3		nylon 1,5	
	model III	model IV	model III	model IV
ΔE_{AM1}	1.6	0.0	0.0	0.8
$\Delta E_{4\text{-}31G}$	1.3	0.0	0.0	0.6
μ_{AM1}	0.55	2.30	0.75	2.57

[a] The model molecules studied correspond to those indicated in Figure 2. ΔE_{AM1} and $\Delta E_{4\text{-}31G}$ refer to the relative energies (in kcal/mol) computed at the semiempirical AM1 and ab initio 4-31G levels, respectively. μ_{AM1} refers to the dipole moment (in D) at the semiempirical AM1 level. The molecular geometries were calculated by optimizing bond lengths and angles using the AM1 method, whereas the torsional angles were kept fixed in the values provided by the LALS refinements (see Table 1).

account. Fortunately, crystals gave a good *hk*0 electron diffraction pattern. Thus, although a 6/*mmm* symmetry is expected for both models, the *R* factor also points clearly to model III.

Relative energies of models III and IV computed for model molecules of nylons 1,3 and 1,5 are showed in Table 3. In agreement with LALS results model III is more stable than model IV for nylons 1,5; but for nylon 1,3 this stability is changed. This deficiency is probably due to the following three reasons. First, the computed conformational energy map $E(\psi_1,\psi_2)$ of *N,N'*-dimethylmalonamide[28] reveals that torsional angles of model IV are close to the minimum of the malonamide residue, whereas those of model III are more distant. Second, recent diffraction results on $CH_3CH_2CH_2NHCOCH_2CONHCH_2CH_2CH_3$[29] show that the dihedral angles ψ_1 and ψ_2 are around 112°, which are similar to the values of model IV. Finally, previous studies demonstrated that crystal environment effects are required for determining the structure of molecules with a high density of polar groups,[31-35] i.e., amide groups. For example, the conformation II of polyglycine (so-called nylon 2) is only obtained when several molecules are included in the model and intermolecular hydrogen bonds with neighboring chains are taken into account.[31-33]

In order to illustrate the latest point, the φ–ψ conformational energy map of the model molecule for nylon 1,3 was computed under the symmetry constraints stated above (see Methods) at the AM1 level. The map is shown in Figure 7. Contour lines are drawn at increments of 1 kcal/mol. The achiral nature of the molecule leads to a Ramachandran-like map with 2-fold symmetry. Moreover, the map is almost symmetric with respect to the line φ = 0° and ψ = 0°. Also it can be noted that the allowable regions of the conformational space for nylon 1,3 are very restricted. These results are in good agreement with those obtained for the retropeptides bis(acetamido)methane ($CH_3CONHCH_2NHCOCH_3$) and *N,N'*-dimethylmalonamide ($CH_3NHCOCH_2CONHCH_3$), where within each compound the angles φ and ψ are energetically related by the chemical symmetry of the residues, i.e., $\varphi_1 = \varphi_2$ in bis(acetamido)methane and $\psi_1 = \psi_2$ in *N,N'*-dimethylmalonamide. Thus, the conformational maps are symmetric with respect the two diagonals in both cases. This situation is completely different from that observed in polyamides derived from ω-amino acids, i.e., without retroamide links, where the angles φ and ψ are energetically independent. As might be expected, due to the absence of packing interactions, none of the allowed regions correspond exactly to one of the models derived from LALS analysis. However, it is immediately obvious from comparison that the model IV conformation is clearly favored with respect to model III. Thus, in the case of nylon 1,3 the stability order between both models changed with respect to the results derived from X-ray data. These results confirm that the presence of neighboring chains is required when the conformation in the crystalline state of molecules with a high density of amide groups is investigated.

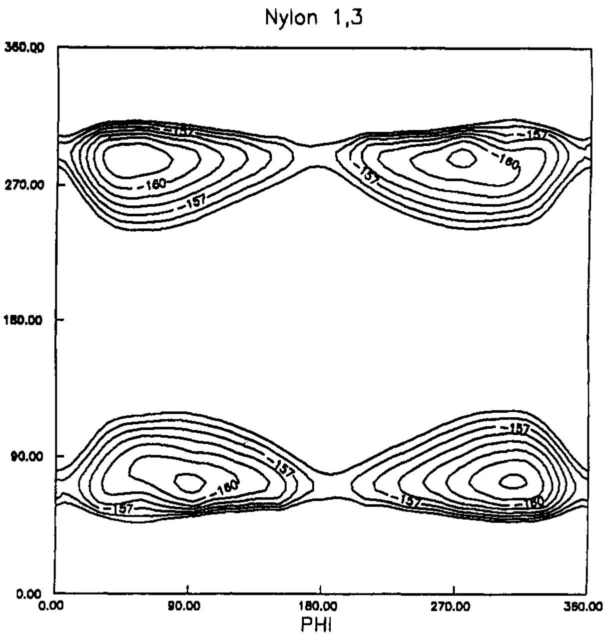

Figure 7. Calculated AM1 energy map for the model molecule of nylon 1,3 when the symmetry constraints $\varphi_1 = \varphi_2 = \varphi_3 = \varphi_4$ and $\psi_1 = \psi_2$ (see Figure 2) are applied. Contour lines with 1 kcal/mol energy difference are represented.

Table 4. Relative Energy Differences (kcal/mol) between the Most Favored Models of the Monoclinic and Hexagonal Forms for Nylons 1,*n*, Where *n* Ranges from 3 to 7

	model II		model III	
nylon	ΔE_{AM1}	$\Delta E_{4\text{-}31G}$	ΔE_{AM1}	$\Delta E_{4\text{-}31G}$
1,3	1.4	3.6	0.0	0.0
1,4	0.0	0.0	0.4	0.7
1,5	1.1	1.2	0.0	0.0
1,6	0.0	0.0	0.3	0.4
1,7	<0.1	0.1	0.0	0.0

The present results indicate that polymers with odd and *n* low values prefer a hexagonal lattice, in agreement with their diffraction data. Thus, in order to ascertain the stability of the 3-fold helical conformation with respect to the monoclinic form found in all other polymers, we carried out quantum mechanical calculations for nylons 1,*n* where *n* ranges from 3 to 7, but comparing models II and III. Results are presented in Table 4. Model II was less stable than model III for nylons 1,3 and 1,5 at both semiempirical AM1 and ab initio 4-31G levels. This could be explained in terms of electrostatic interactions. Thus, in model II the close amide groups are in a parallel orientation, whereas in model III they are in opposite directions. This correlates well with the AM1 dipole moments for models II and III, which are respectively 3.52 and 0.55 D for nylon 1,3 and 3.22 and 0.75 D for nylon 1,5. When the number of methylene units is odd and low, the conformation of model II becomes polar due to the parallel orientation of the amide groups (see Figure 3c). On the contrary, the hexagonal model III induces a low dipole moment which seems to stabilize the conformation. On the other hand, model II was more stable than model III for nylons 1,4 and 1,6. In a similar way, the conformation with the lowest dipole moment seems most favorable. Thus, the AM1 dipole for models II and III are respectively 0.00 and 2.95 D for nylon 1,4 and 0.00 and 1.92 D for nylon 1,6.

Similar calculations were performed for nylon 1,7. In this case, the 3-fold helical conformation proposed in model III was more stable than model II by approximately 0.1 at both AM1 and ab initio 4-31G levels. These results seem to suggest that when the number of methylene units increases, the monoclinic packing is stabilized. Indeed, the energy difference predicted for nylon 1,7 is so small that it could be easily compensated by the packing interactions between the different molecules in the crystal if they were taken into account. Consequently, the threshold value for the stabilization of the monoclinic packing with respect to the hexagonal one for nylons 1,*n*=odd should be predicted at a value of *n* equal or greater than 7.

Discussion

The conformations of several members of the nylon 1,*n* family have been studied using LALS and quantum mechanical methodologies. X-ray and electron diffraction experimental data for nylons 1,5 and 1,6 were taken into account, and the results were extrapolated to the remaining polymers. The calculations presented here show that nylons 1,*n* have a different conformation depending on the *n* value. Thus, calculations reveal a monoclinic packing for polymers with an even *n* value, whereas polymers with a low and odd *n* value adopt a hexagonal one.

In the case of nylon 1,6 LALS analysis points to a new structure which has the same torsional angles for the isolated methylene group that have been observed in some methylene diamides.[26] Furthermore, quantum mechanical calculations for nylons 1,4 and 1,6 reveal that the conformation based on a γ form is clearly unfavored with respect to this. More specifically the torsional angles of the isolated methylene group for the γ form fall into a completely disallowed zone of the conformational energy map of the bis(acetamide) residue.[19] Thus, our results indicate that when we have an even number of methylene units between two amide groups, the relations $\varphi_1 = -\varphi_2 = -107.7°$ would place the amide groups with parallel orientation, whereas $\varphi_1 = \varphi_2 = 87.5°$ would place the amide groups in opposite orientation, the latter being clearly favored by attractive electrostatic interactions. This is an important finding, since it is the first time that a structure of this type has been observed in aliphatic polyamides.

Regarding polymers with a low and odd *n* value, experimental data for nylon 1,5 show a hexagonal conformation. LALS and energy calculations for nylon 1,5 point clearly to a helical structure with a 3-fold screw axis. However, for nylon 1,3 energy calculations are not sufficient to discern between the two possible models. This must be attributed to the high ratio between amide and methylene groups, which make then accounting of interactions with neighboring molecules essential. Thus, in a recent SCF–MO study of the polyglycine II structure (nylon 2) several authors found that packing interactions play a key role in determining the accessibility of the 3_1 conformation.[31–33] When the crystal environmental effects were not included in the calculations, the experimental conformation of the polyglycine II did not correspond to a stationary point of the conformational energy surface, and it is unfavored from an energetic point of view. Indeed, we can think of nylon 1,3 as polyglycine, in which every other amide group has opposite direction:

...–$NHCH_2CONHCH_2CONHCH_2CO$–... polyglycine

...–$NHCH_2NHCOCH_2CONHCH_2NH$–... nylon 1,3

The torsional angles of the polyglycine II structure are close to those of model III for nylons 1,3. The energy map computed for the model molecule of nylon 1,3 indicates that the results found for the polyglycine II conformation[30] could be extended to nylon 1,3. Thus, crystal environment effects are required for determining the structure of molecules with a high density of amide groups.

What is clearly apparent is that the conformational angles φ_1 and φ_2 provided by the LALS procedure for the favored models (models II and III for the monoclinic and hexagonal packing forms, respectively) are in good agreement with those found in a recent study for nylons 1,*n* in general.[19] In that work a quantum mechanical study of the preferred conformations of the bis(acetamido)-methane, which is the basic unit of nylons 1,*n*, was performed. Thus, calculations "in vacuo" provided only two enantiomeric minima with the same energy, and the torsional angles were $\varphi_1 = \varphi_2 = \pm 67°$. However, when the crystal environmental effects were included in the calculations, the torsional angles changed approximately 15°, and the new values were $\varphi_1 \approx \varphi_2 \approx \pm 80°$. This particular conformation of the isolated methylene unit seems to agree with experimental data independent of the *n* value.

These calculations allow us to reach two important conclusions: (a) from an energetic point of view, the 2/*b* symmetry conformation is the most favored for nylons with an even *n* value, whereas the 3-fold helical form is favored for polymers with a low and odd *n* value; (b) in general, the energetic results are in good agreement with those provided by the LALS analysis, although the packing interactions do have a significant influence on the structure of nylon 1,3.

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