Structure of a Cyclic Trimer as a Model of Nylon 11. Folding at Lamellar Surfaces

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ABSTRACT: We have studied by single-crystal X-ray diffraction the structure of a cyclic trimer model of nylon 11 (IUPAC name: 1,13,25-triazacyclohexatriacontane-2,14,26-trione). The crystal is organized in layers of hydrogen-bonded rings similar to nylon lamellar crystals. The rings fold both at the amide and methylene regions. Neighbor layers show van der Waals contacts among similar turns, either methylene/methylene or amide/amide. A new type of fold has been found, which includes an amide group and a methylene unit. Such folds may coexist in nylon lamellar crystals with conventional turns similar to the β-turn found in proteins. The orientation of up and down chains in the crystal is different from the orientation usually assumed for nylon 11, which suggests an alternative unit cell for nylon 11. We also include an analysis of the vertical displacement of hydrogen bonded layers found by different authors in nylon 11, which shows that it may vary between zero and three methylene units. In the trimer crystal we find a displacement of two methylene units.

Introduction

The structure of some of the common polyamides, such as nylon 6,6, appears to be rather well established, although some structural details are still controversial.[1,2] On the other hand there are many reports[3−14] on the odd-numbered polyamides with contradictory results, as will be discussed below. Furthermore, the surface structure of lamellar crystals of polyamides has also been the subject of different publications,[15−21] but little direct information on that matter is available. Of particular interest is the recent work of the Bristol group[20,21] with short oligoamides, which shows that depending on their length they may fold at either the alkane or amide units.

In view of this situation, it appeared of interest to study in detail the structure of cyclic polyamides. Recently we have studied the structure of cyclic dimers related to nylon 11[22,23] and to nylon 12.[24] In this paper we report the structure of a trimer model[25] of nylon 11, which provides additional information on the surface structure of polyamide crystals. Furthermore, it provides a model for the organization of polymer chains in nylon 11 which helps to understand the contradictory results on this polyamide which we have mentioned above.

Experimental Section

The cyclic trimer was obtained as described[22] from the low molecular weight byproducts in the industrial synthesis of nylon 11 (Rilsan). The mixture of oligomers was first extracted in methanol and then fractionated by liquid chromatography: semipreparative HPLC, Spherisorb C18, 250 × 20 mm S5 ODS 2, using aqueous acetic acid (5 mM)−methanol (20:80, v/v) as eluent and a flow rate of 7 mL min^{-1}. Elution was monitored using an UV detector at 210 nm. The peak corresponding to the title compound was identified as trimer by mass spectroscopy.

The crystals were grown by vapor diffusion at room temperature from sitting drops. The best crystals were obtained from a mixture of formic acid and dioxane as solvent/precipitant, respectively. Drops containing 89% dioxane were equilibrated against a reservoir with 95% dioxane. The crystals were long and thin platelets. They were unstable when removed from their mother liquor. Because of their small size, the diffraction pattern could not be recorded in a conventional difractometer. For that reason data were collected using synchrotron radiation at the beamline DW22 in DCI LURE Outstation on a 345 mm MAR Research image-plate scanner.

For data collection, crystals were mounted on a fiber loop and then flash cooled at 100 K in a cold nitrogen stream using an Oxford Cryosystems Cryostream. Two sets of data were collected at resolution cutoffs 2.3 and 1.02 Å in order to avoid saturation of the high-intensity reflections. A half-sphere of reflections was measured in order to improve the averaged intensity values. Data were processed and reduced with DENZO and SCALEPACK.[26] It is important here to note that the new version of DENZO was essential in order to process more than one image at a time. We added either 5 or 10 frames for high and low resolution, respectively. The overall R_{merge} for all data after scaling and merging was 2.8% and data were 92.9% complete in the resolution range 40−1.02 Å. Crystal and diffraction data are given in Table 1.

The structure was determined by direct methods using SHELXS and refined with SHELXL, both programs being included in the SHELX-97 package.[27]

All non-H atoms were refined anisotropically. Methylene hydrogen atoms and those bonded to N atoms were included at calculated positions. All hydrogen atoms were refined with geometrical constrains (ride model) and isotropic temperature factors. No additional geometrical constrains were needed for non-H atoms. Atomic coordinates and displacement parameters are given in Table 2.

Results and Discussion

Structure of the Trimer Ring. The structure of the ring as determined by X-ray diffraction is shown in Figure 1. It is organized as two extended chains with turns in the upper and lower part of the figure. Both extended chains are practically all trans, although small differences from 180° are present. The largest deviations are found in the bonds placed next to the peptide groups. The bend at the alkane end is similar to that found in cyclic parafins, with gauche bonds at the turns. The

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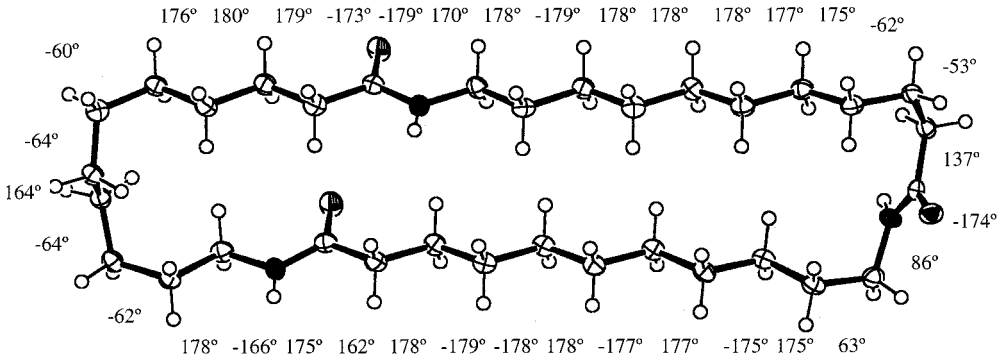

Figure 1. Conformation of the crystallized trimer ring. The torsion angles are indicated. Nitrogen atoms are black and oxygen atoms are hatched.

Table 1. Crystal and Structure Refinement Data for the Trimer Ring

Crystallographic Data	
$C_{33}H_{63}N_3O_3$	synchrotron radiation
$M_r = 549.86$	$\lambda = 0.9637$ Å
monoclinic	rotation per frame: 3°
$P2_1$	total rotation = 180°
$a = 5.41(6)$ Å	$T = 100$ K
$b = 7.9940(10)$ Å	
$c = 37.522(11)$ Å	
$\beta = 93.843$ (10) deg	
$V = 1618$ (17) Å^3	
$Z = 2$	
$d_{calcd} = 1.129$ Mg m^{-3}	R_{sym} (overall/last shell) = 0.028/0.082
completeness: 92.9%	
resolution range = 40−1.02 Å	$h = 0 \rightarrow 5$
2612 measured reflections	$k = 0 \rightarrow 7$
1639 independent reflections	$l = -36 \rightarrow +36$
1635 reflections with $I > 2\sigma(I)$	
Refinement Results	
refinement on F^2	
$R[F^2 > 2\sigma(F^2)] = 0.03$	$\Delta\rho_{max} = 0.119$ e Å^{-3}
$WR(F^2) = 0.08$	$\Delta\rho_{min} = -0.146$ e Å^{-3}
1639 reflections	
353 parameters	

bend at the other end shows an unexpected geometry, since it includes a CH_2 unit next to the amide group. In the cyclic dimer rings of nylon 11[23] and nylon 12[24] there is only the amide group at the turn. A more detailed comparison will be presented below.

The peculiar structure of the amide turn shown in Figure 1 is quite unexpected, it results in a distortion of the ring. In fact is possible to construct a ring with parallel aliphatic chains at both sides of the ring and just the amide group at the turn, as it is found in dimer rings.[23,24] In such rings the amide groups at both sides move to the same height and their dipole moments are at a short distance. Furthermore, hydrogen bonding with neighbor rings is not adequate. In summary, it appears that the overall conformation of the ring is chosen in order to optimize the interactions of the amide groups while mantaining an adequate packing of the aliphatic chains.

The rings are organized in layers as shown in Figure 2. The surfaces of the layers create van der Waals contacts between either the aliphatic or amide turns. Thus, in the crystal there is an apolar interface among aliphatic chains and a polar interface among the amide groups. At the apolar surface of contact one row of trimers interdigitates with the next, as is clearly apparent in Figure 2. Amide groups in the polar interface are oriented in opposite directions so that their dipole moments cancel.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)
O(1)	13168(4)	4135(3)	3475(1)	31(1)
O(3)	16712(4)	8471(3)	3200(1)	33(1)
O(2)	−503(4)	3000(3)	296(1)	28(1)
C(11)	11733(5)	5340(4)	3477(1)	22(1)
C(10)	11955(5)	6635(4)	3769(1)	26(1)
C(9)	14257(6)	6450(4)	4022(1)	26(1)
C(8)	14484(5)	7785(4)	4311(1)	26(1)
C(7)	16784(5)	7608(4)	4568(1)	24(1)
C(6)	17146(5)	9010(4)	4844(1)	27(1)
C(5)	17419(5)	10768(4)	4691(1)	24(1)
C(4)	19739(5)	10981(4)	4481(1)	26(1)
C(3)	19736(5)	12516(4)	4239(1)	25(1)
C(2)	17701(5)	12491(4)	3931(1)	25(1)
C(1)	17961(5)	11037(4)	3675(1)	25(1)
N(1)	15930(4)	11058(3)	3398(1)	24(1)
C(33)	15414(6)	9749(4)	3186(1)	24(1)
C(32)	13114(6)	9887(4)	2932(1)	26(1)
C(31)	13016(5)	8665(4)	2624(1)	25(1)
C(30)	10660(5)	8794(4)	2378(1)	24(1)
C(29)	10533(5)	7569(4)	2070(1)	24(1)
C(28)	8254(5)	7711(4)	1815(1)	24(1)
C(27)	8190(5)	6517(4)	1500(1)	24(1)
C(26)	5940(6)	6728(4)	1234(1)	25(1)
C(25)	5940(5)	5595(4)	910(1)	26(1)
C(24)	3792(5)	5919(4)	635(1)	24(1)
C(23)	3866(5)	4916(4)	292(1)	26(1)
N(3)	3692(4)	3109(3)	352(1)	23(1)
C(22)	1534(5)	2296(4)	362(1)	23(1)
C(21)	1677(5)	462(4)	461(1)	25(1)
C(20)	−290(5)	−7(3)	723(1)	23(1)
C(19)	−243(5)	1088(4)	1054(1)	25(1)
C(18)	2172(6)	1017(4)	1291(1)	25(1)
C(17)	2251(6)	2239(4)	1602(1)	26(1)
C(16)	4559(6)	2148(4)	1849(1)	25(1)
C(15)	4659(6)	3409(4)	2152(1)	27(1)
C(14)	6971(6)	3271(4)	2405(1)	26(1)
C(13)	7177(6)	4561(4)	2704(1)	26(1)
C(12)	9553(6)	4320(4)	2934(1)	25(1)
N(2)	9917(4)	5533(3)	3221(1)	23(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The structure of the crystal is further stabilized by a network of hydrogen bonds, which is most clearly apparent in Figure 3. Hydrogen bond parameters are given in Table 2. Each ring is hydrogen bonded with four of its neighbors. Hydrogen bonds among the internal amide groups have a polar orientation; they are all parallel and oriented in the same direction. The hydrogen bonds among the amide groups at the surface are oriented at an angle of about 60° from those inside the rings. They are a little strained, as is apparent from Table 3.

A stricking feature of this crystal is its polar nature. All molecules have the same stereochemistry. Thus, the

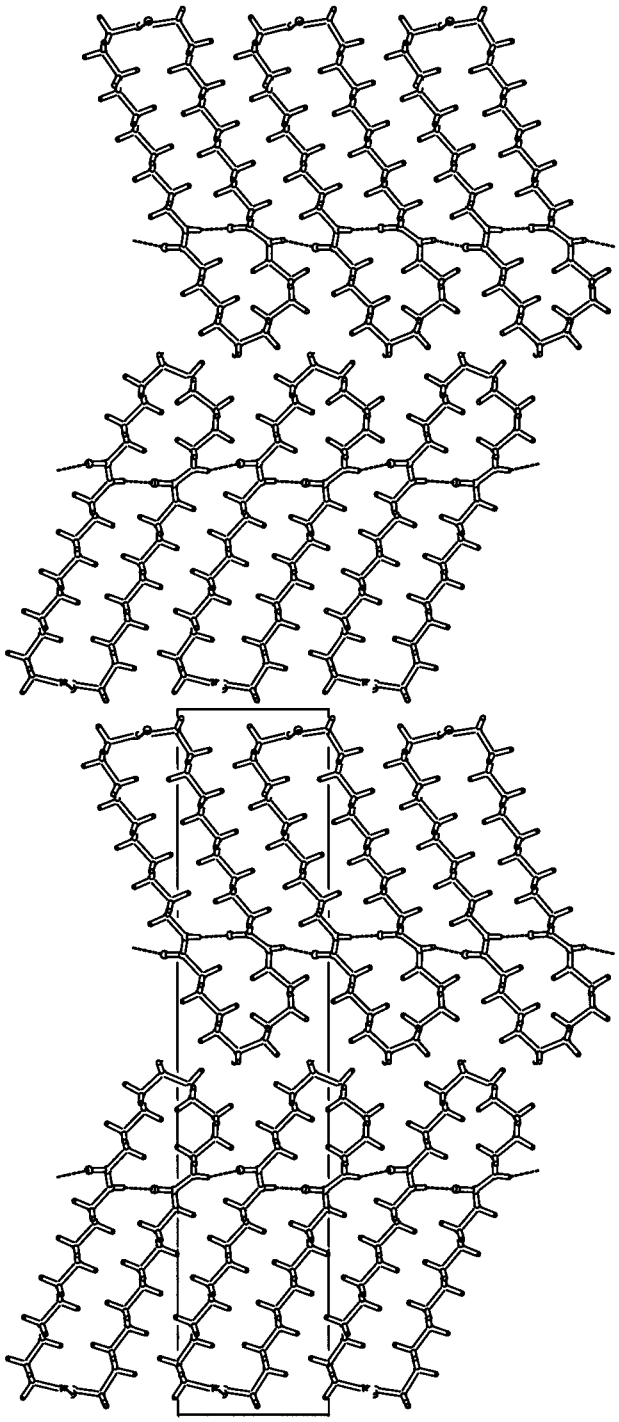

Figure 2. Projection onto the *yz* plane of the trimer rings in the crystal. The outline of a unit cell is shown. Hydrogen bonds are indicated as dashed lines. An additional set of hydrogen bonds runs perpendicular to the plane of the figure at the amide turn of the rings. Amide turns are at the center and at both ends of the figure. The rings do not lie flat on the plane of the paper.

rings in an individual crystal have the same chirality, although there are no asymmetric carbons in the molecular rings. In the other oligoamide rings which have been studied, it is common to find half or whole molecules which are mirror images, whereas in the trimer ring presented here all molecules have the same chirality. Obviously individual crystals may either have the conformational angles reported here or their opposites.

Table 3. Hydrogen-Bonding Distances in Å for the Trimer Ring[a]

D−H···A	D−H	H···A	D···A	D−H···A
N1−HN1···O1^{i}	0.860	2.071	2.902	162.1
N2−HN2···O3^{ii}	0.860	2.058	2.916	175.6
N3−HN3···O2^{iii}	0.860	2.476	3.160	136.9

[a] Key: i and ii, amide groups in the straight sides of the ring; iii, amide group at the bend of the ring

Table 4. Unit Cell Dimensions of Nylon 11 (Å and deg)

	a	*b*	*c*	α	*β*	*γ*
trimer derived structure[a]	9.65	5.41	14.92	62.2	90	55.65
Dosière and Point (form II)[8]	9.8	5.25	14.9	50.5	90	72

[a] At 120 K.

Structure of Nylon 11 Derived from the Trimer Crystal. The crystal structure we have described is determined by all 36 atoms in the ring. However, with the exception of the five atoms in the turns, all other atoms are organized as parallel chains as it is most clearly seen in Figure 3. In fact a possible structure for nylon 11 can be derived from the crystal structure of the cyclic trimer by elimination of the five atoms in the turns. Thus, a nylon 11 structure is generated as shown in Figure 4a. Additional views are presented in Figure 4, parts b and c. The derived unit cell is given in Table 4.

The organization of nylon 11 as presented in Figure 4, and Table 4 has features in common with the unit cell usually accepted[8] for nylon 11 but also some important differences. Hydrogen-bonded polymer chains have opposite orientations as shown in Figure 4b, a feature not found in the original model suggested by Slichter.[4] However this feature is now generally accepted by most authors, since it is most easily compatible with chain folding in lamellar crystals of this polymer. An additional feature of the trimer crystal is that all polymer chains in the crystal have the same orientation of their hydrogen bonds, so it is not necessary to use a doubled unit cell with layers of hydrogen bonded chains in opposite orientations, as suggested by Hasegawa et al.[13]

Consecutive layers of hydrogen-bonded sheets are displaced by two CH_2 units, as it is clearly apparent in Figure 4c. This situation is different from nylon 6,6 in the α form,[1] which has a similar organization. In the latter case a displacement of three CH_2 groups is found. As a result the α angle of the unit cell of nylon 11 given in Table 4 (62.2°) is clearly larger that the value found in nylon 6,6 (48.5°).[1] This feature of nylon 11 is also in disagreement with theoretical calculations[28] which would also predict a displacement of three CH_2 units among neighboring planes. This question will be further discussed below.

A significant (and subtle!) difference of the unit cell given in Table 4 with that used by most authors stems from the fact that they have chosen a cell analogous to that used for nylon 6,6. As a consequence the cell usually accepted implies that neighbor layers will have the polymer chains in different orientations from those found in the trimer. A comparison between the two unit cells is shown in Figure 5. In the structure derived from the trimer ring, chains 1 and 3 go up while chains 2 and 4 go down. If the alternative unit cell is chosen,[8] based on the unit cell used for the α form of nylon 6,6, then chains 1 and 4 should go up, while 2 and 3 go down. We think that this feature of the trimer structure is maintained in nylon 11. Thus, the unit cell given in

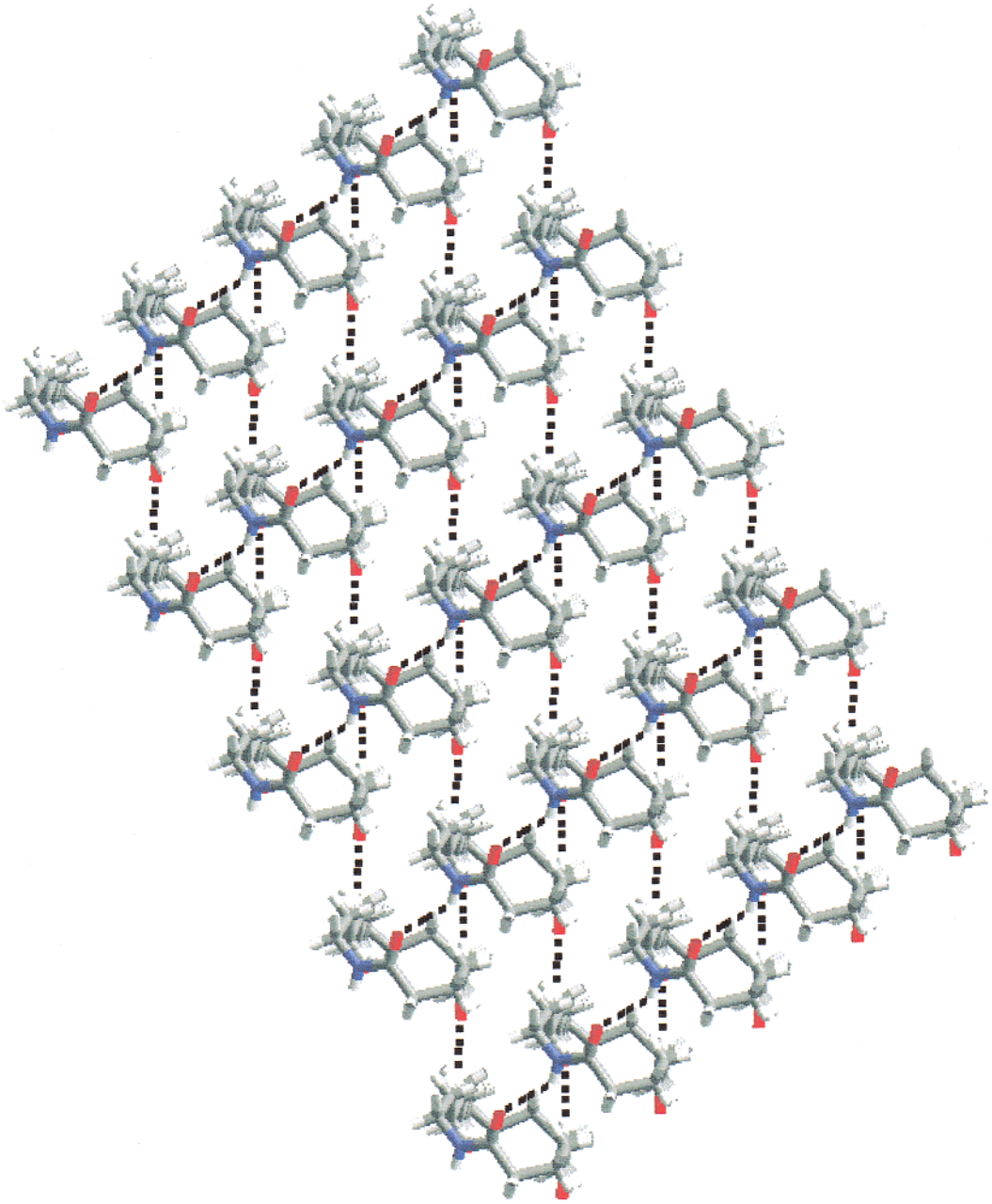

Figure 3. View of a set of trimer rings projected onto a plane perpendicular to the direction of the methylene chains. Oxygen atoms are shown in red and nitrogen atoms in blue. Hydrogen bonds among the internal peptide groups appear in the vertical direction, whereas those among the amide groups at the turns appear in an oblique orientation. Note that each ring forms hydrogen bonds with four of its neighbors.

Table 4 for the trimer derived structure should be used, with the limitations that we will discuss below. The difference in the γ angle with the cell used by Dosière and Point[8] as given in Table 4 is mainly due to this difference in the orientation of polymer chains in neighbor layers.

The change of unit cell suggested by our experimental results is fully compatible with the electron and fiber diffraction data in the equatorial plane[3−13,29] available in the literature, only the indices of the reflections have to be changed. The cell given in Table 4 for the trimer derived structure corresponds to an alternative choice of a unit cell for nylon 6,6, since in the triclinic crystal system equivalent alternative unit cells may be chosen.

In the case of the α form of nylon 6 and other even nylons, the unit cell usually accepted[30] is similar to the standard cell of nylon 11. Unfortunately there is no direct experimental evidence on the relative orientation of polymer chains in neighbor layers. Thus, it is possible that the unit cell of nylon 6 should also be changed[31] if the relative polarity of chains turns out to be like that in the trimer ring. In fact, a recent theoretical analysis[32] has shown that a statistical mixture of both cells might be present in nylon 6.

In the unit cell shown in Figure 4a the plane of the amide groups lies in the *xz* plane, with hydrogen bonds oriented in the *x* direction. However the aliphatic carbons do not lie in this plane and form an angle with it which oscillates between 12 and 19°. This setting angle optimizes the van der Waals interactions of methylene hydrogen atoms as it can be appreciated in Figure 4a. Such a rotation of the aliphatic carbons has also been suggested[1,2] for nylon 6,6, and has been found in a low molecular weight model[33] of the latter nylon.

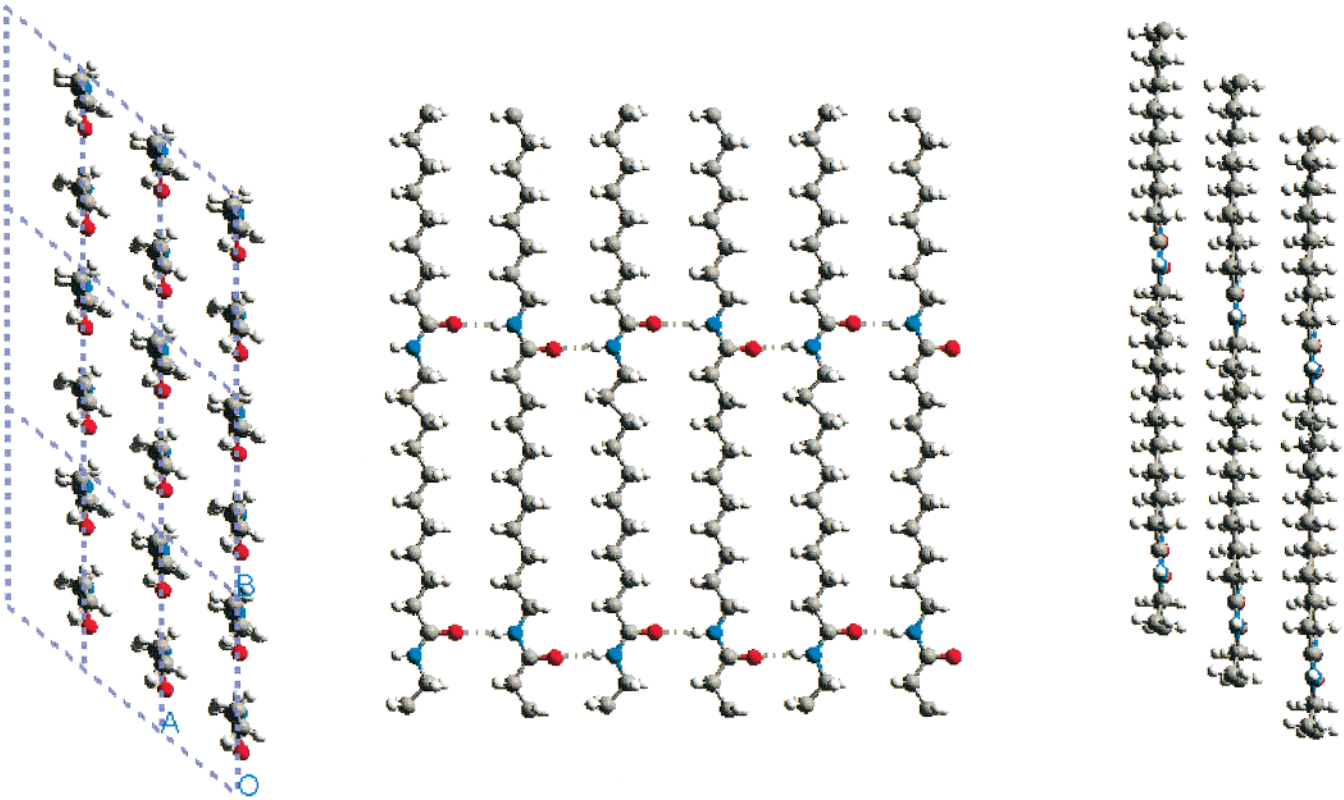

Figure 4. Model of nylon 11 obtained from the crystallized ring structure by eliminating the atoms at the turns: projected onto the *yx* (a), *xz* (b), and *yz* (c) planes. Oxygen atoms are shown in red and nitrogen atoms in blue. Note that the direction of the coordinate axes is different from Figure 2.

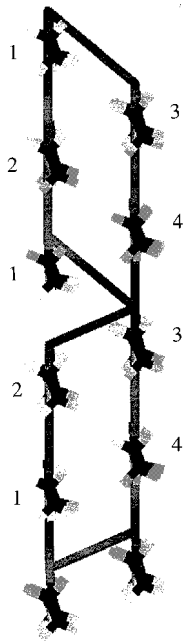

Figure 5. Unit cell of nylon 11 as derived from the trimer ring is shown in the upper end of the figure in the same orientation as in Figure 4a. The conventional unit cell[8] is shown at the bottom. In the first case chains 1 and 3 run up, while chains 2 and 4 run down. In the conventional unit cell chains 1 and 4 run up, while chains 2 and 3 run down.

All experimental results available for the usual triclinic form of nylon 11 are consistent with the projection of either of the unit cells shown in Figure 5. The organization of polymer chains results in two equatorial reflections at about 3.75 and 4.4 Å spacings, typical for the α form of nylons. Electron diffraction data from lamellae of odd nylons[7,29] are also consistent with such organization of hydrogen bonded chains. In the trimer derived unit cell the equatorial spacings should appear at 3.70 and 4.35 Å, somewhat smaller values due to the fact that the data have been collected at 120 K.

The unit cell derived by us for nylon 11 can be compared with experimental data by considering the meridional reflection found in fibers of nylon 11. As it is apparent from Table 5 this value depends on the way the sample has been prepared, as it can be ascertained

Table 5. Meridional Spacing (Å) Found in Nylon 11 Samples Prepared by Different Authors[a]

	d_{001}	CH_2	ref
extended chain	15.0	0	
trimer derived structure (calcd)	12.3	2	this work
Slichter (calcd)	11.2	3	4
Chen et al.	11.3	3	9
Sasaki	11.3/14.7	3/0	6
Kawaguchi et al. (triclinic cell)	11.3	3	7
Kim et al.	11.3−12.5	3/2	10
Dosière and Point	11.6/12.8	3/2	8
Zhang et al.	11.8	2.5	13
Wu et al.	11.9	2.5	11
Mathias et al.	12.1	2	12
Hasegawa et al. (calcd)	12.6	2	14
Aelion	13.3/14.1	1	3
Little (calcd)	14.1	1	5
Kawaguchi et al. (monoclinic cell)	14.9	0	7

[a] Notes: The values given for d_{001} correspond to those experimentally measured from either fibers or films. In some cases,[7,8] crystal mats were also used. Two values are given when the authors have found two different structures. When only the unit cell is reported, d_{001} has been calculated. The CH_2 column indicates the approximate vertical displacement of molecules in neighbor planes in the *y* direction as discussed in the text.

in the quoted references.[3−13] Only in some cases a value close to that expected for the trimer derived model is found. In most cases the d_{001} spacing is smaller, in the range 11.2−11.6 Å, which indicates that the hydrogen-bonded sheets are shifted by a larger amount than in Figure 4c. As a result the α angle diminishes, as shown in Table 4, and the displacement of neighbor hydrogen-bonded sheets increases to about three methylene groups, as found in nylon 6,6[1] and as predicted by theory.[28] In some other cases the d_{001} spacing approaches the value for the fully extended chain, which indicates that in those samples the peptide groups on the average lie at the same height, there is no progressive shift of hydrogen-bonded layers as that shown in Figure 4c. It appears therefore that in nylon 11 the vertical shift of neighbor layers may vary significantly (between zero and three methylene groups) as the conditions used to prepare the sample are changed. The approximate number of methylene groups shifted in each case is also given in Table 5 (CH_2 column).

A further puzzling feature of the experimental data obtained from oriented fibers and crystal mats of nylon 11 is that the (001) reflection very often has a meridional orientation. Regular crystals with plane shifts such as those shown in Figure 4c should give an off-meridional reflection. Furthermore, in electron diffraction experiments[29] all equatorial reflections are often present, a feature not consistent with lamellar crystals having inclined polymer chains. It appears therefore that nylon 11 crystallites respect the position of neighbor polymer chains as shown in Figure 4, parts a and b, but the shift in the vertical direction (Figure 4c) may be highly variable, with frequent twinning along different crystal planes.

Chain Folding in Lamellar Crystals of Polyamide. Early studies[15] on polyamide folding showed that in nylon 6,6 the folds should occur in the methylene segments in order to maintain the crystal structure. More recently it has been found[16,17] that some polyamides must fold at the amide group, as predicted from its stereochemical features.[34] In Figure 6 we present the folds found in the trimer ring together with other folds previously described.[23,24] Similar folds have been found by other authors[35−37] in low molecular weight ring compounds. A γ-turn has also been suggested in synthetic polypeptides.[38] Folding in lamellar crystals of even−even nylons has also been analyzed in detail.[39] Most of these folds are similar to the various types of turns found in proteins.[40] An exception is the fold in the trimer ring reported here, which includes a methylene group in the turn. There is no a priori reason which should favor one type of fold over the other types. In fact it is likely that different types of fold might be present in individual polyamide crystals, since their edges are usually very irregular.[7,16−20,29,41,42] It is often assumed that polymers fold along a crystallographic plane and thus give rise to straight crystal edges, but this does not appear to be the general case in polyamide crystals. The regular structure found at the surface of the trimer ring crystals (Figure 3) might suggest that nylon lamellar crystals could also have a regular surface. However it is likely that defects are common and different types of fold may coexist in any real crystal. In fact, twinning is very common[29] in odd-numbered nylons.

An important difference between the chain folds found in the trimer crystal and those suggested by the Bristol group[15,20,21] is that the latter authors assume that folding occurs in the same plane as hydrogen bonding among the nylon chains, whereas in our case folding takes place in a different direction, as it is most clearly apparent in Figure 3. If polymer lamellar crystal do fold as in the trimer ring, they should not have regular edges, as experimentally found.

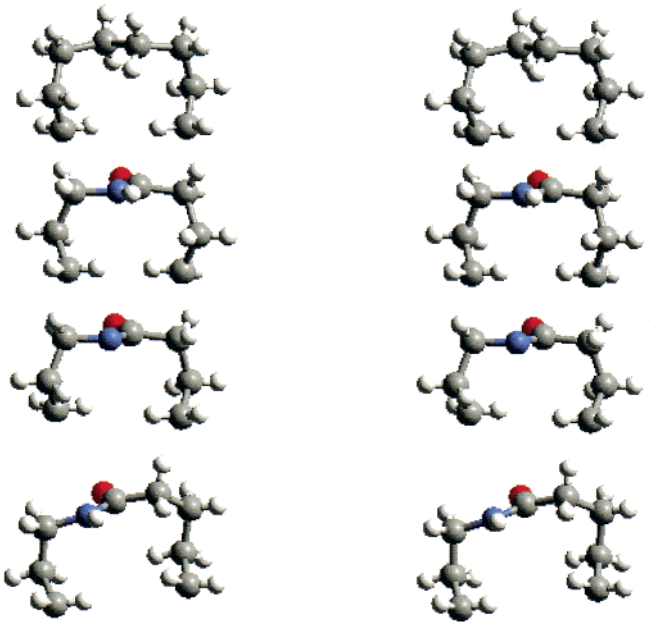

Figure 6. Stereoviews of some of the turns found in oligoamide rings. From top to bottom: methylene turn in the trimer ring; turn in a hydrated dimer[23] of nylon 11; turn in the acid form[22] of the dimer of nylon 11; amide turn in the trimer ring. The three upper examples are also found in other cycloalkanes[44] and oligoamides.[35−37] Mirror images of all these turns are also possible.

If amide groups are present in the surface of polyamide lamellar crystals, they should form hydrogen bonds with neighbor amide units. Such a network may be present locally, but it will probably not extend to the whole surface of the crystal. In particular, some chains may fold at the methylene segments and disrupt hydrogen bonding at the surface of the crystals. The nature of the crystal surface is a question of practical importance, since water absorption may depend on the number of structural defects at the surface: water molecules will preferentially interact with unsatisfied hydrogen bonds.

Conclusions

The study of oligoamide rings provides information for an understanding of folding at the surface of lamellar crystals. From the work reported here, it appears that folding at the amide groups may be favored in polyamides in general, as it was already suggested by the studies of Dale[34] on macrocyclic compounds. A new type of fold has been discovered, which includes a methylene unit. Previous work[22−24] demonstrated folds similar to the β-turn in proteins, which only involve the amide group. Thus, folding at the crystal surface may use different geometries (Figure 6) and may occur in different directions, thus explaining the irregular sides usually found in lamellar crystals of polyamides.

The coexistence of different types of folds at the surface of polyamide crystals may also be accompanied by other irregularities, such as cilia, longer folded chains lying on the surface, etc. Frequent twinning is also a

source of disorder. All these irregularities may contribute to explain the anomalous large amount of amorphous material found in real polyamide samples,[43] including nylon 11.[13]

Our studies suggest an alternative structure for nylon 11. They indicate that the up and down orientation of polyamide chains usually assumed might need to be modified, as demonstrated in Figure 5. A similar change might also be necessary for the α form of nylon 6, although no experimental results are available on that question.

In the trimer ring neighbor chains are displaced by two methylene units (Figure 4c), whereas in nylon 11 this displacement varies between zero and three methylene units, depending on sample preparation, as demonstrated in Table 5.

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