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Polymorphism in nylon 66

M. L. COLCLOUGH*
Metallurgy and Materials Science Department, Imperial College of Science and Technology, London, UK

R. BAKER†
Chemistry Department, University College, Gower Street, London, UK

The molecular structure of room temperature (RT) nylon 66 and its transition to the high temperature (HT) form have been examined by X-ray crystallographic techniques. An initial literature survey on the RT form revealed a number of anomalies in the spatial relationships of the molecules within the unit cell, namely, poor ethylenic segment packing, distortion of the amide group from a planar configuration and lack of similarity on the projected cell base between RT nylon 66 and RT nylon 6. These anomalies have been resolved, and models proposed which give a better fit between calculated and observed data. The remainder of the paper describes the examination of the HT form with the object of determining whether or not a three-dimensional hydrogen bonded network could exist beyond 180° C. By determining unit cell dimensions and measuring intermolecular hydrogen bond distances it was possible to eliminate certain directions for hydrogen bonded planes. On the basis that any such distance must not exceed about 0.31 nm, which is the maximum hydrogen bond distance reported in the literature, it was concluded that a three-dimensional network could not exist. The cause of the structural transition is attributed to progressive changes in ethylenic segment torsion angles.

1. Introduction

Polyhexamethylene adipamide (nylon 66) undergoes a gradual structural transition when heated from 20° C to 160° C. The room temperature form has a triclinic unit cell [1]. No cell parameters have been published for the high temperature form, although it has been tentatively classified as pseudohexagonal [2, 3]. Suggestions have been made [4] that rotations of the polymer chains about their long axes on heating cause the transformation. An alternative model for the molecular motion has been proposed by Brill [2] and Schmidt and Stuart [3], who considered that rotational molecular jumps of 60° could occur at high temperatures, giving rise to a three-dimensional hydrogen bonded network. The purpose of this paper is to present new X-ray diffraction data on the high temperature form and to determine which of these models best explains the observations.

Published information [4] indicates that the transformation is not only gradual and continuous, but is reversible, so that a natural starting place for the structure determination of the high temperature form would be the room temperature triclinic form. Bunn and Garner [1] state that a number of apparently minor disagreements exist between the experimental data and that generated by their model of nylon 66. In addition conflicting evidence, which will be discussed later, casts doubt about the position of the molecule within the unit cell, and on the distortion of the amide group. Consequently the initial part of this paper is devoted to resolving the conflicting evidence on the structure of room temperature nylon 66. The final part of this paper discusses the three-dimen-

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[*] Present address: Imperial Chemical Industries Ltd., Paints Division, Slough, Berks., UK.
[†] Present address: University of London Computer Centre, Guildford Street, London, UK.

sional hydrogen bonded network and shows how its existence is unlikely in view of the unit cell geometry derived from experimental high temperature X-ray films. These findings support the conclusions reached by Cannon *et al.* [5], who used optical techniques to examine the transition.

2. Low temperature nylon 66

2.1. Experimental

Good definition X-ray fibre patterns were obtained from an axially oriented nylon 66 monofilament of draw ratio 6, which had been immersed in a 7% solution of phenol in water, boiled for 2 h in water, and finally dried in air at 65° C for 3 days. The specimen was under tension for the whole cycle. The density of the fibre was $1.16\,\mathrm{g\,cm^{-3}}$.

All the observed reflections on the fibre pattern were indexed using the Bernal [6] reciprocal lattice technique. The calculated unit cell dimensions agreed with those of the triclinic α form [1]. Unfortunately, due to crystallite disorientation along the fibre axis, only 36 of the many reflections were suitable for quantitative estimation of intensity obtained from radial and azimuthal density profiles.

Two large and intense reflections (0 1 5) and the overlapping (1 1 7) (1 2 7) were observed at the intersection of the meridian and the fifth and seventh layer lines. The indexing technique indicated that they were not diatropic, which was confirmed by tilting experiments. Due to inaccuracies in measuring and scaling the intensities of these two reflections they were not included in the structure modelling exercise.

2.2. Data reduction

Of the 36 reflections whose integrated intensities were measured, 20 were of the multiple type – common in fibre patterns – which meant that the normal technique of directly comparing the agreement between calculated and observed structure factors had to be slightly modified. The observed intensities were divided by the relevant value of the Lorentz polarization factor, giving an observed structure factor amplitude squared term (Fo^2). The computer programs employed, generated structure factor amplitude squared terms (Fc^2) for individual reflections, and so no problem exists in the comparison of such individual terms for any proposed model. However, many of the observed reflections, as stated, overlapped, so to obtain a meaningful comparison the individual $|Fc^2|$ terms have to be "overlapped" or summed for the model data. For example $|Fo^2|_{(0\,1\,0)+(1\,1\,0)}$ has to be compared to $|Fc^2|_{(0\,1\,0)} + |Fc^2|_{(1\,1\,0)}$ in the residual factor equation which follows:

$$R = \frac{\Sigma(|Fo^2| - |Fc^2|)}{\Sigma|Fo^2|}, \qquad (1)$$

where R is the residual factor.

2.3. Structure modelling

Any molecular model used to generate structure factor amplitudes for comparison with observed values is subject to certain restraints. They are principally the limitations imposed by the atomic species present, by their bond angles and lengths, and by the geometry of the unit cell. Bunn and Garner [1] paid particular attention to these features; in addition it is considered that for polyamides, the plane-like qualities of the amide group, and also the molecular packing should be deemed to be of equal importance.

Concerning the selection of carbon–carbon–carbon (C–C–C) bond angles, two approaches were adopted. The first assumed that the tetrahedral bond angle of 109°28′ – as found in diamond – predominated in the backbone chain. When plotted orthogonally, using Pauling and Corey's data [7] for the dimensions of the amide group, a molecular repeat distance of 1.72 nm was obtained, which agreed with the experimentally

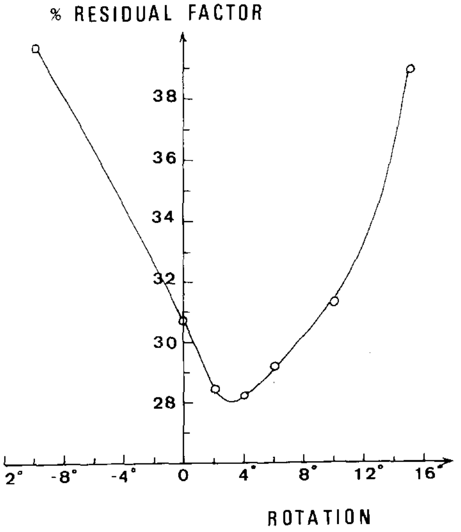

Figure 1 Effect of the angular rotation of a planar nylon 66 molecule, initially lying in the (0 1 0), on the residual factor.

observed value. By means of a short computer program the orthogonal co-ordinates were rotated about the chain axis through various angles, and triclinic co-ordinates output. The X-ray 70 computer program package was used to generate $|Fc^2|$ values for each angular change. After a scale factor correction, residual factors were calculated using Equation 1. The residual factor was plotted against angle of rotation. Fig. 1 shows this plot, where a zero rotation indicates a molecule lying in (0 1 0). An anticlockwise rotation looking down the *c*-axis onto the projected cell base is classed as positive.

To assess the significance of this residual factor minimum, shown in Fig. 1, Bunn and Garner's atomic co-ordinates were used to generate structure factors which were compared to our observed values. The percentage residual obtained was 43.1%. A significant improvement over this is obtained for the 4° rotated planar molecule, $R = 28.3\%$. The atomic co-ordinates for this molecule are given in Table I. The observed, reduced data is given in Table II, with the corresponding $|Fc^2|$ values.

The second approach to the selection of C–C–C bond angles was suggested by an examination of published data on long chained molecules, [7–9]. The C–C–C bond angle was rarely 109°28′, a more acceptable average being 111°. If however, an orthogonal plot is made of such a molecule, the overall chain axis length extends to approximately 1.75 nm. Changing bond lengths within permitted levels of accuracy makes only a slight change in this dimension. Although the accuracy of measuring lattice parameters on a fibre pattern is not high, a difference between 1.72 nm and 1.75 nm is discernible. Consequently torsion angle changes have to be postulated to reduce the molecular repeat distance to 1.72 nm. Even if the limitation is observed that the amide group is planar, there are still a large number of torsion angle changes which could give rise to the necessary shortening. Manipulation of CPK models indicated that not only did changes in the torsion angles adjacent to the amide group shorten the chain axis, but also improved the packing of the ethylenic segments of the molecule. The torsion angles changed were C2–C3–N1–C4 and C4–N1–C3–C2, and the changes made were of equal amount, but in opposite senses, so that an extended chain configuration was maintained.

The torsion angle of the group of atoms C2–

TABLE I The atomic fractional coordinates of the 4° rotated molecule with C–C–C bond angle 109°30′ (Model 1)

Atom	*x*	*y*	*z*
Carbon 1	−0.100	0.012	0.038
Carbon 2	0.078	−0.009	0.108
Carbon 3	−0.139	0.017	0.184
Carbon 4	−0.161	0.019	0.328
Carbon 5	0.061	−0.007	0.387
Carbon 6	−0.111	0.013	0.469
Nitrogen 1	−0.005	0.001	0.247
Oxygen 1	−0.407	0.049	0.184

TABLE II The observed and calculated structure factor amplitude squared terms for the 4° rotated molecule with carbon bond angles of 109°30′ (Model 1) and for the molecule with a 9° torsion angle change (Model 2)

Index (*h k l*)	$\lvert Fo^2\rvert$	$\lvert Fc^2\rvert$	
		Model 1	Model 2
(1 0 0)	2539	2026	2248
(0 1 0) (1 1 0)	8762	8485	8279
($\bar{1}$ 1 0) (2 1 0)	923	1176	1432
(2 0 0)	261	386	547
(1 2 0)	1145	1247	966
(0 2 0) (2 2 0)	1715	2488	2337
(3 1 0)	336	1	11
(3 2 0)	481	19	16
(1 3 0)	168	726	483
(0 3 0) (3 3 0) ($\bar{3}$ 1 0) (4 1 0)	355	1195	1079
($\bar{1}$ 0 1)	1408	538	552
(0 0 2)	165	165	132
(0 1 2) (1 1 2)	95	324	395
(0 $\bar{1}$ 2) (2 1 2) (1 2 2)	127	232	133
(0 0 3) (0 1 3)	470	304	298
($\bar{1}$ 0 3)	136	219	202
($\bar{1}$ 1 3)	129	198	171
($\bar{1}$ $\bar{1}$ 3)	75	110	110
(1 1 4)	34	55	48
(1 2 4)	54	73	50
(2 1 4) (2 2 4)	286	320	350
(1 1 5)	104	58	93
(0 0 5) (1 2 5)	120	140	98
($\bar{1}$ 1 5) (0 2 5) ($\bar{1}$ 0 5)	131	249	287
($\bar{1}$ 1 6)	269	333	341
(2 2 6) ($\bar{1}$ 0 6)	406	556	618
(2 1 6)	202	213	179
(1 1 7) (0 2 7)	983	1031	863
($\bar{1}$ 1 7) (2 2 7)	825	1108	1037
(2 3 7) ($\bar{1}$ 0 7) ($\bar{1}$ 2 7) (2 1 7)	1565	1761	1661
(1 0 7) (0 3 7)	560	750	480
($\bar{2}$ 1 7) ($\bar{2}$ 0 7) (3 2 7)	1186	1351	1296
(2 0 7) ($\bar{1}$ 3 7) ($\bar{2}$ 2 7) (3 1 7)	577	1416	1530

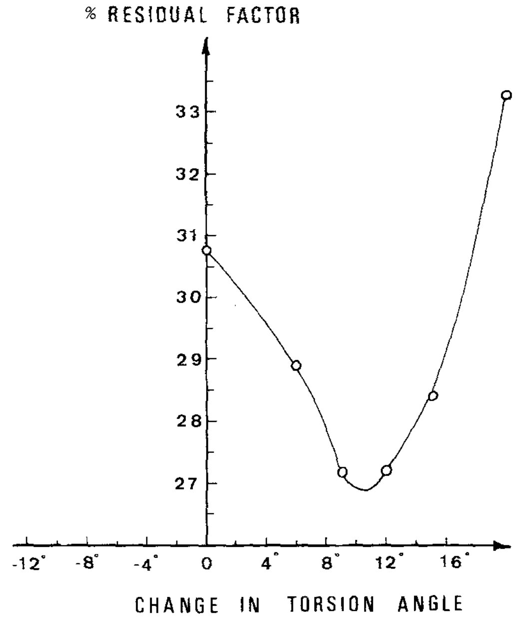

Figure 2 Residual factor dependence on the simultaneous change in the torsion angles adjacent to the amide in nylon 66.

C3–N1–C4 is defined as the angle through which the plane C3–N1–C4 is viewed from the direction C2–C3. This torsion angle was rotated in steps in clockwise and anticlockwise directions, while C4–N1–C3–C2 was simultaneously rotated in anticlockwise and clockwise directions. For each step change in the two torsion angles, atomic co-ordinates were output, which were then rotated 4° from the (0 1 0). Fig. 2 shows a plot of the resulting residual factors versus the combined torsion angle change. Negative torsion angles on this figure indicate that C2–C3–N1–C4 was rotated anticlockwise, and C4–N1–C3–C2 clockwise.

A minimum occurs in the plot at a residual factor of 27.2% for a 9° torsion angle change.

TABLE III The atomic fractional co-ordinates of the 4° rotated molecule with C–C–C bond angle 111° and a 9° torsion angle change of the bonds adjacent to the amide group

Atom	*x*	*y*	*z*
Carbon 1	−0.0954	−0.0027	0.0421
Carbon 2	0.0623	0.0181	0.1037
Carbon 3	−0.1361	0.0168	0.1865
Carbon 4	−0.1454	−0.0234	0.3374
Carbon 5	0.0542	−0.0059	0.3887
Carbon 6	−0.0966	−0.0156	0.4789
Nitrogen 1	0.0052	−0.0189	0.2527
Oxygen 1	−0.4027	0.0497	0.1871

The atomic co-ordinates for this model are listed in Table III. The corresponding values of $|Fc^2|$ are contained in Table II for the purpose of comparison with Model 1 data.

2.4. Discussion

There are three important differences between the two models proposed here and the one suggested by Bunn and Garner [1]. The first of these concerns the plane-like qualities of the amide group, which, as previously described, was used as a structure modelling constraint. Pauling and Corey [7] consider that the amide bond dimensions are indicative of a partial double bond structure which stabilizes a planar configuration. Extensive experimental evidence, taken from a wide range of amide-containing molecules is presented in support of their sug-

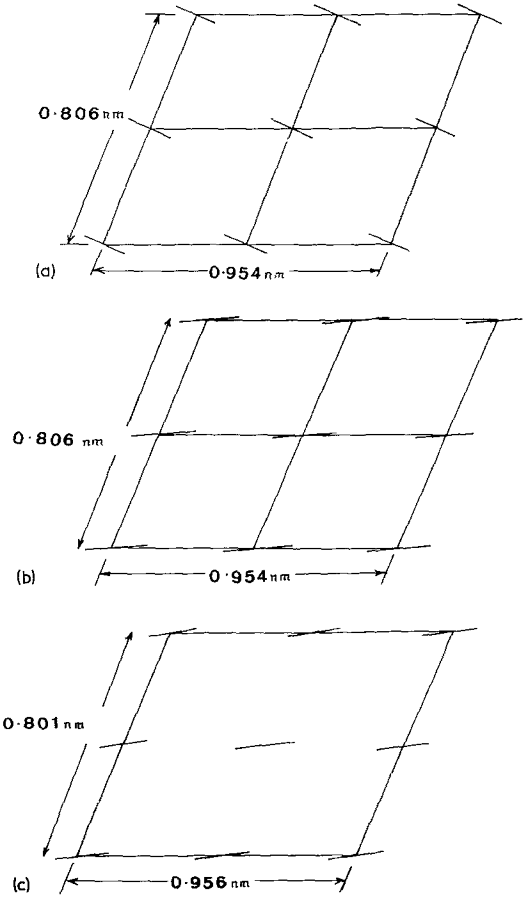

Figure 3(a) Projected basal plane of nylon 66 [1]. Four unit cells are shown. (b) Projected basal plane of nylon 66 according to the authors. Four unit cells are shown. (c) Projected basal plane of the unit cell of nylon 6 according to Holmes *et al.* [9].

gestion. Northolt and Alexander [8,9] also refer to the inherent plane-like qualities of the amide group in their work on the cyclic monomer of nylon 66 and cyclic dimer of nylon 6. Consequently the assumption that the amide group is planar was considered a valid one, which is supported by an improved residual factor for both models.

The second important difference concerns the location of the molecule within the unit cell, which can be demonstrated clearly by reference to projections on the unit cell base. Three such projections are shown in Fig. 3, which compares the projected cell bases of the first model presented here with those of Bunn and Garner for nylon 66, and Holmes, Bunn and Smith [10] for nylon 6. The latter authors used a somewhat similar technique in solving the structure of nylon 6; they rotated a $(h0l)$ reciprocal lattice net on a one-dimensional Fourier transform of the molecule, and read off structure factors for the various orientations. A minimum in their plot of residual versus angle of rotation for their planar molecule occurred at a rotation of $\sim 7^\circ$ towards the long diagonal on the projected cell base, which agrees closely with the molecular positioning presented in this paper for nylon 66. The similarity between the two molecules and between their dimensions on the projected cell base, as shown in Fig. 3, strongly indicates that there should be close correspondence between their molecular positioning and their intermolecular packing. The 4° rotated molecule is in keeping with this observation.

The third important difference concerns the intermolecular packing of hydrogen bonded amide groups and the ethylenic groups linking them. The role of hydrogen bonding in determining the β unit cell angle and "a" parameter spacing has been described [1] and its very important role in elevating the melting point of aliphatic polyamides is well known. However, in accommodating these strong cohesive hydrogen bond forces, the linking ethylenic segments must distort from a planar configuration, since not to do so means that ethylenic segments occupy the same space. In the first model presented here, a rotation of 4° of the planar molecule is seen when transmitted to CPK models to improve the ethylenic chain packing. This is shown schematically in Figs. 4a and b, where a small improvement can be seen.

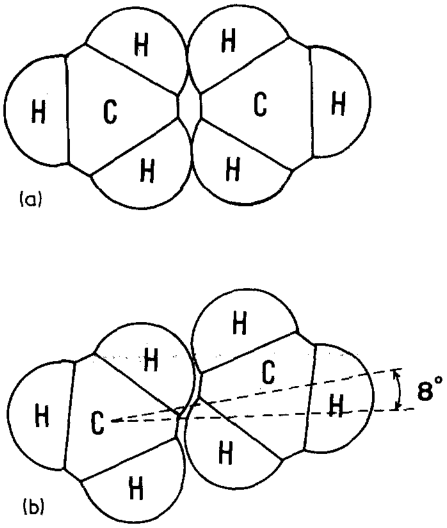

Figure 4 Schematic diagrams showing the improvement in packing of adjacent carbon chains with rotation about an axis normal to the plane of the paper. (a) Planar molecules lying in the (0 1 0). (b) Planar molecules each rotated 4° out of the (0 1 0).

Closer packed structures, such as the β Trilaurin [11] can only be achieved by movement in the chain axis direction, i.e. a shift normal to the paper in Fig. 4, so that carbon atoms on adjacent molecules do not directly face one another. The improvement in ethylenic group packing is seen as the reason for the rotation of the planar molecule towards the long diagonal for both nylon 66 and nylon 6, and on a similar basis could be predicted to occur for nylon 6.10.

To further improve ethylenic group packing, movement is required in the chain axis direction, which is effectively what happens when torsion angles are changed. If the C–C–C bond angles are also considered greater than 109°30′ then torsion angle changes can be made which will bring the long chain axis length back to 1.72 nm and improve the packing. The C–C–C angle chosen was 111° because it commonly occurs in long chained molecules. There are a large number of torsion angle changes and combinations of change which could shorten the 111° molecule from 1.75 nm to the acceptable value of 1.72 nm. Unfortunately there is not enough X-ray data for a least-squares analysis, nor additional data from other sources to indicate which torsion angles change. Consequently the simplest situation was considered, where rotation of the torsion angles adjacent to the amide group were seen to improve the packing of the CPK models. The plot of torsion angle change versus residual once more showed a minimum. The significance of the residual factors as this minimum is approached is complicated by the changing length of the molecule, since a minimum is likely to occur at 1.72 nm for many molecular arrangements as the rotations change the length of a molecule from 1.75 nm to say 1.70 nm. However, the minimum which occurred appeared at a slightly lower residual than was previously found by the planar molecule rotation technique, and since very much lower than that for the structure suggested by Bunn and Garner, may be considered a valid alternative.

A further consequence of this out-of-plane distortion is that it provides an answer to the query raised by Bunn and Garner on the packing of the hydrogen bonded planes in the ⟨0 1 0⟩. For a planar molecule there is no reason for one molecule to adopt a $3c/14$ displacement along the c-axis as opposed to a $5c/14$ or a $7c/14$ displacement with respect to its neighbour. However, the torsion angle changes generate zig-zag layers, which have very limited positions in which to pack. With the torsion angles selected here $3c/14$ is the only acceptable position for the packing, since, as shown schematically in Fig. 5, a $5c/14$ (or $7c/14$) position results in ethylenic segments trying to occupy the same space. This situation only being resolved by a change in the unit cell dimensions.

If attempts are made to construct the nylon 66 β phase [1] by successive up-down displacement of adjacent chains, then interference of a similar nature occurs. The torsion angle model therefore provides indirect support for Keller and Marradudin's [12] work, who consider that the layer line streaking and additional reflections, which normally occur in fibre patterns of nylon 66, are not caused by a different phase, but by a macroscopic interference effect.

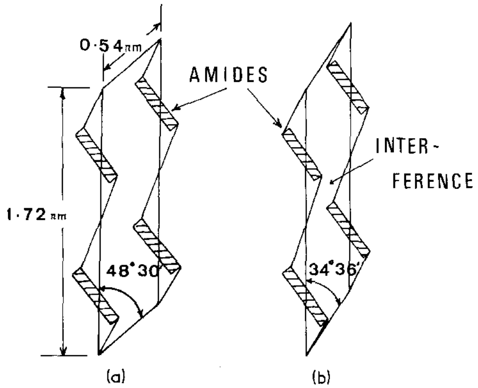

Figure 5 (a) Schematic diagram of the packing of two adjacent molecules in the ⟨0 1 0⟩ which shows how a $3c/14$ translation is necessary for the zig-zags to pack together. (b) Schematic diagram of two adjacent molecules with a $5c/14$ translational difference. In the centre of the diagram the ethylenic part of the molecules interfere and try to occupy the same space.

It should be stated, however, that any torsion angle change or combinations of change which satisfy the unit cell data and result in a non-planar molecule, severely limit the position in ⟨0 1 0⟩ of adjacent $3c/14$ hydrogen bonded sheets and prevent the β phase formation.

Cannon [13], from infra-red spectra and chain length studies on nylons 55, 56, and 57, concludes that full association of amide groups is achieved at the expense of disordering the hydrocarbon segments. Moreover, from the fine structure CH_2 spectra he deduces that this disordering is non-random. These statements lend support to the torsion angle model proposed in this work, in that nylon 57 is remarkably like nylon 66 in the number of fully associated amide groups, and in chain length, and yet shows a small amount of hydrocarbon disorder. Unfortunately Cannon does not specify the nature of the non-random disordering of the hydrocarbon segments, but it is conceivable that a rotation of the torsion angles adjacent to the amide group would create such a non-random effect.

2.5. Conclusion

In the results section two structural solutions have been presented. The experimental data strongly support the planar molecule rotation model as a starting place for further atom position refinement. The second model presents one such refinement, based on torsion angle changes, which give an improved overall picture. Confirmation of which torsion angles do change, if any, and by how much, can only be obtained with a larger data set and a least-squares analysis. The problem of reflections (3 1 0) and (3 2 0) which consistently calculate too low may also be resolved.

3. High temperature nylon 66

3.1. Introduction

With increasing temperature the asymmetric packing in the basal plane of the triclinic cell is considered to shift towards hexagonal packing [4]. The transformation is characterized by the convergence of the spacings of two very intense equatorial reflections (0 1 0) and (1 0 0) together with a decrease in the length of the chain axis. In the room temperature form, the hydrogen bonds act as intermolecular spacers, so that on the projected cell base the "*a*" parameter has the relatively large value of 0.48 nm. The hydrogen bonded sheet packing distance "*b*" is, however, only 0.41 nm. On heating "*b*" gradually increases to 0.48 nm, which is indicative of intersheet hydrogen bonding, and led Brill [2] and Schmidt and Stuart [3] to postulate the existence of a dynamic three-dimensional hydrogen bonded network.

In an attempt to verify this postulate Olf and Peterlin [14] predicted quantitatively the effect of two motional mechanisms – rotational oscillation and 60° molecular jumps, which they termed the "60° flip-flop" – on the anisotropy of the nuclear magnetic resonant second moment in axially oriented nylon 66. Their predictions were compared to experimental second moment data. Unfortunately they found it impossible to distinguish between the two types of motion for the paraffinic portion of the molecule. They did not discount, however, the possibility that amide groups might perform the "60° flip-flop" and generate a three-dimensional network.

This paper adopts a crystallographic approach, since the molecular motion of whatever type must occur within the limits set by the dimensions of the unit cell as they transform from the low to high temperature values. Consequently the main experimental objective was to obtain values for the high temperature lattice parameters. A second objective was to obtain integrated intensity data, in order to give an indication of the motion of the molecules within the unit cell.

TABLE IV Comparison of film measured ζ_m values with those obtained by graphical indexing with $\gamma^* = 120°$ (ζ_g)

Index	ζ_m	ζ_g
(0 1 0) (1 0 0) (1 1 0)	0.36	0.36
(2 1 0) $(1\,\bar{1}\,0)$	0.63	0.63
(2 0 0)	0.72	0.72
$(2\,\bar{1}\,0)$	0.95	0.95
(0 0 1)	0.06	0.07
(1 1 1)	0.32	0.32
(1 2 1)	0.55	0.55
(0 0 2)	0.13	0.13
(0 1 2)	0.22	0.23
(1 1 2)	0.28	0.29
(0 0 3)	0.19	0.19
$(\bar{1}\,0\,3)$	0.35	0.36
(2 1 3)	0.60	0.61
(1 2 3) (1 0 3)	0.45	0.45
(0 0 4) (1 1 4)	0.27	0.26
(1 2 4)	0.36	0.37
(1 0 4) $(\bar{1}\,0\,4)$ (0 2 4)	0.52	0.50
(0 0 5) (1 2 5)	0.32	0.33
(1 2 6) (1 1 6)	0.25	0.29
(0 0 6)	0.38	0.39
(2 2 6)	0.51	0.53
$(\bar{1}\,1\,7)$	0.43	0.43
(2 0 7)	0.50	0.51
(1 0 7)	0.64	0.65

3.2. Experimental

The high temperature X-ray fibre pattern was obtained on a specially designed, temperature controlled X-ray camera with torroid optics for improved focusing. The fibre specimen, prepared as previously described, was kept under constant load for the exposure at 170° C to prevent heat relaxation, and in vacuum to prevent oxidation.

Twenty six reflections were clearly distinguished from the relatively high level of background normal scatter. The reflections were indexed using the Bernal [6] reciprocal lattice technique. Using this technique it was clear that all crystal systems except triclinic could be excluded as a basis for indexing, because of the absence of 90° cell angles. Table IV shows the close agreement with ζ values measured on the X-ray film, and those obtained by the Bernal graphical indexing procedure. An alternative indexing system could not be found – apart from a system with $\gamma^* = 60°$ as opposed to $\gamma^* = 120°$ – consequently it was assumed that the unit cell was triclinic, but of unknown symmetry, since the fibre pattern automatically creates a centre.

Calculation of cell dimensions based on $\gamma^* = 120°$ gave a real space cell, whose dimensions were recognizably a modification of the room temperature ones. Plots in the spacing change of (0 1 0) and (1 0 0) with increasing temperature indicated that no sudden structural transformation occurred, so that the assumption that the two cells are closely related appears valid.

Table V compares the room temperature and high temperature unit cell dimensions.

TABLE V Comparison of room temperature (RT) and high temperature (HT) unit cell dimensions

Dimension	HT nylon 66	RT nylon 66
a	0.5 nm	0.49 nm
b	0.59 nm	0.54 nm
c	1.623 nm	1.72 nm
α	56°40′	48°30′
β	80°36′	77°
γ	59°52′	63°30′

TABLE VI Comparison of $|Fc^2|$ values with the observed data for the amide group of the high temperature form, rotated through 10° towards the long diagonal on the projected cell base

Index ($h\,k\,l$)	$|Fo^2|$	$|Fc^2|$	Scale factor
(0 1 0) (1 0 0) (1 1 0)	114 079	4112	27.7
(2 1 0) $(1\,\bar{1}\,0)$	1 558	265	5.8
(2 0 0)	684	152	4.5
$(2\,\bar{1}\,0)$	154	114	1.3
(0 0 1)	13 156	560	23.5
(0 0 2)	15 740	616	25.5
$(\bar{1}\,0\,3)$	840	88	9.5
(1 1 4) (0 0 4)	646	72	8.9
(2 0 7)	778	30	25.9

Of the 26 observed reflections only 9 were good enough to warrant integrated intensity measurements which were subject to the data reduction procedure.

3.3. Data reduction

As for the room temperature fibre pattern, the problem of overlapping reflections occurred. It was solved in a similar way, however, due to the lack of data it was not possible to immediately derive a scale factor which would put the observed structure factor amplitude onto the same absolute scale as the Fc. Consequently the level of agreement between $|Fo^2|$ and $|Fc^2|$ terms had to be monitored by means of the scale factor.

3.4. Structure modelling

The work of Olf and Peterlin indicated that thermal vibration effects and torsion angle changes occurred on heating, one superimposed onto the other. This combination will tend to smear out the X-ray contributions from atoms engaged in such motion, so that an increasingly diffuse pattern will emerge. It was therefore considered that the greatest contribution to the sharply defined reflections would come from the amide group, which, because of its plane-like qualities, would not be involved in torsion angle changes, and as a unit less susceptible to thermal effects.

A planar amide group was moved up and down the c-axis in the (0 1 0) and $|Fc^2|$ values output for reflections (0 0 1) and (0 0 2). The best position for the amide group was decided by scale factor refinement. The scale factor agreement was further improved by rotating the amide group about its new position. A rotation of 10° towards the long diagonal on the projected cell base gave the best result. Moreover, the agreement was also good for two other intense reflections – (0 1 0) (1 0 0) (1 1 0) and (2 0 7). The agreement for the other reflections was poor as indicated in Table VI.

For the molecule in this position the hydrogen bond spacing was 0.311 nm.

Similar nearest neighbour calculations were performed with the amide group lying in the (0 1 0) and in the (1 0 0). The distances were 0.311 nm and 0.35 nm respectively. By tilting the amide groups with respect to the c-axis in each of these planes the carbon–nitrogen distance could be reduced to 0.288 nm in the (0 1 0) but in the (1 0 0) the value always increased.

3.5. Discussion

The existence of a three-dimensional hydrogen bonded network in the high temperature polymorph was proposed on the grounds that the projected cell base was hexagonal and the basal spacings reminiscent of hydrogen bonded planes. NMR and other studies failed to confirm or deny the existence of such a network. However, optical studies [5] on drawn and rolled fibres of nylon 66 at 20° C and 220° C indicated that despite some loss in fibre orientation, on heating they remained optically biaxial. If the amide groups were randomized or had formed a three-dimensional network the fibre should have become optically uniaxial. Cannon concludes that the network therefore does not exist at high temperatures. The approach adopted in this work – which confirms the findings of Cannon [5] – is simple and based upon geometric considerations. If the nearest neighbour spacing at either extremity of the "60° flip-flop" is the same and within the acceptable limits of hydrogen bond spacing, then this would provide further support for the network theory. If, however, they are greatly different or outside the acceptable limits then the network is very unlikely to exist.

The experimental evidence indicates quite clearly that although the spacing of the planes on the projected cell base in the ⟨0 1 0⟩ is reminiscent of hydrogen bonded planes, the minimum nitrogen–oxygen spacing of 0.35 nm is not. Consequently the three-dimensional hydrogen bonded network is thought not to exist. The evidence also confirms that the preferred direction of the hydrogen bonds is, as for the room temperature form, approximately in the ⟨1 0 0⟩ with a nearest neighbour distance of 0.311 nm between the nitrogen and oxygen atoms.

The quantitative experimental intensity data, although limited, tends to confirm that an acceptable position for the amide group should lie in or close to the (0 1 0) with the hydrogen bond direction close to ⟨1 0 0⟩.

The support provided by the intensity data is as stated, meagre and open to some doubt, since the positions of the non-amide carbon atoms and their contributions to the X-ray diffraction pattern have not been considered. The strength of this case lies with the determination of the unit cell parameters and the assumption that the amide group – wherever it is positioned – remains substantially planar as the temperature is raised. The first of these points has been covered in the experimental section. The effect of high temperatures, although increasing the individual atom vibration within the amide group, is unlikely to convert the Sp^2 hybrid bonds to the more easily rotatable Sp^3 or to induce large out-of-plane oscillations. Furthermore, infra-red evidence [15, 16] indicates that on a time average all hydrogen bonds remain intact up to the melting point, which means that the spatial relationship between intermolecular oxygen and nitrogen, and therefore interatomic oxygen and nitrogen, is at least similar to the room temperature relationship. Consequently the assumption, in keeping with studies elsewhere [7–9], that the amide group remains substantially planar, appears reasonable.

3.6. Conclusion

The initial work on the room temperature form of nylon 66 established that torsion angle changes of the non-amide carbon atoms, though small, could account for most of the anomalies observed by Bunn and Garner. From information on the HT structure it is possible to propose mechanisms for the molecular motions which cause the transition to occur.

Starting with the non-planar RT molecule, a gradual increase of the amide associated (C2–C3–N1–C4 and C4–N1–C3–C2) torsion angles with temperature can be seen to cause the required unit cell lattice parameter changes. With reference to Fig. 5, an increase in these torsion angles will decrease the molecular chain axis repeat length, and will increase the sharpness of the zig-zags as well as the "*b*" unit cell dimension. Moreover, a further effect of the increased sharpness is that the intersheet packing must change and α become increasingly obtuse to accommodate it. These unit cell changes could occur without influencing the "*a*" dimension of the unit cell which is dominated by hydrogen bonds. The torsional oscillation of the hydrocarbon segments described by other workers [13, 14, 17] could take place serving to augment the chain axis dimension decrease and the "*b*" axis increase.

A further consequence of this torsion angle change is that to maintain a continuous chain structure the amide groups have to rotate, effectively pivoting about the hydrogen bond direction. Cannon [13] considers that since the CONH infra-red frequencies are sensitive to changes in the association of amide groups, any statistical distribution of amide–amide contact distances or of the angle between adjacent dipoles should lead to a broadening of the absorption bands. The spectra of nylon 66 [13] shows such a broadening with increased temperature, which Cannon attributes to amide rotation caused by the twisting motions of the hydrocarbon segments. The X-ray data presented in this work on the position of the amide group at high temperatures (although limited) indicates that a change in amide position and therefore change in angle between adjacent dipoles has occurred. A simple picture emerges of the heat-induced transformation being driven by the twisting motions of the ethylenic segments, which cause the torsion angles adjacent to the amide group to change. This in turn causes the amide groups to rotate, the total effect giving rise to the observed crystallographic dimension change.

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