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Model Compounds of Aromatic Nylons. 2. Study of *N*,*N'*-Trimethylenebis(*p*-methoxybenzamide), *N*,*N'*-Pentamethylenebis(*p*-methylbenzamide), and *N*,*N'*-Heptamethylenebis(*p*-methylbenzamide) by X-ray Diffraction, IR Spectroscopy, and ^{13}C CP/MAS NMR Spectroscopy

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ABSTRACT: In order to establish the conformation of poly(trimethyleneterephthalamide) or 3T nylon and of the parent pentamethylene (5T nylon) and heptamethylene (7T nylon) polyamides, three model compounds, the X-para-substituted *n*-methylenedibenzamides (n = 3, X = OMe; n = 5, 7; X = Me), were synthesized and characterized by X-ray diffraction, infrared spectroscopy, and solid-state CP/MAS ^{13}C NMR. All three compounds show comparable conformations for the $CONH(CH_2)_nNHCO$ sequence of atoms. They are τgtt, τgtttt, and τgtttttt for n = 3, 5, and 7, respectively (g = gauche $\simeq 60°$, t = trans $\approx 180°$; $\tau \approx 80$–$90°$). Although chemically symmetrical, the extreme torsion angles of the molecules differ by $\simeq 90°$. The pentamethylene- and heptamethylenebis(*p*-methylbenzamide) molecules are held through four hydrogen bonds to two other distinct molecules, thus forming ribbons extending parallel to a unit-cell edge. On the other hand, trimethylenebis(*p*-methoxybenzamide) forms hydrogen bonds with four other molecules. All these H bonds are almost linear. The N–H···O angles vary between 159° and 172°, while the N···O distances range from 2.84 to 2.96 Å. As expected, the amide V bands in the infrared spectra of penta- and heptamethylenebis(*p*-methylbenzamide) are clearly split. This observation is in agreement with the observed disymmetry of the molecules. An analysis of the ^{13}C CP/MAS solid-state NMR spectra of the model compounds of 3T nylon confirms the structure proposed for this polyamide.

Introduction

In the first article of this series, we investigated the crystalline structure of nT nylons, or poly(oligomethyleneterephthalamides), with an odd number of methylene groups using X-ray diffraction, conformational analysis, model compound study, and IR spectroscopy. The X-ray fiber diagrams of 3T and 5T nylons were of such poor quality that neither the unit-cell dimensions nor the space group could be obtained without ambiguity. Nevertheless, an approximate value of the fiber repeat was obtained for $n = 3$ and 5. On the basis of these values and taking into account the conformational analysis, two plausible chain conformations were proposed.[1]

In this second article, we introduce the use of CP/MAS ^{13}C NMR spectroscopy. It is our hope to determine in which way this technique can bring new information on the conformation of the polymers. It has been shown, from the study of the spectra of a number of model compounds of 4T nylon,[2] that various effects can induce changes in the chemical shift of the atoms. Therefore, it is preferable to record the spectra of more than one model compound for which the structure is known in order to investigate the different parameters that may affect the chemical shift before attempting the interpretation of the spectra of a polymer with respect to its conformation.

We have determined the crystal structure of three new model compounds, namely *N*,*N'*-trimethylenebis(*p*-methoxybenzamide), abbreviated 3DBN-*p*-OMe; *N*,*N'*-pentamethylenebis(*p*-methylbenzamide), or 5DBN-*p*-Me; and *N*,*N'*-heptamethylenebis(*p*-methylbenzamide), or 7DBN-*p*-Me. The NMR spectra of 3DBN, 5DBN, and 7DBN and those of the above model compounds were recorded in order to verify that the factors affecting the chemical shifts may be quantified, as was the case for models of 4T nylon[2] and for other nDBN's.[3]

Experimental Section

The syntheses of the model compounds are similar to that of 2DBN.[4] The polymers were synthetized according to Shashoua and Eareckson.[5] Single crystals of the model compounds, in the form of lamellae, were obtained by recrystallization from ethanol–water solutions. The space groups and lattice parameters were measured on a NONIUS CAD-4 diffractometer (3DBN-*p*-OMe, orthorhombic, a = 9.857 (2) Å, b = 18.585 (9) Å, c = 18.715 (4) Å, space group *Pbca*; 5DBN-*p*-Me, triclinic, a = 5.0561 (9) Å, b = 5.1286 (9) Å, c = 35.926 (6) Å, α = 88.14° (1°), β = 88.16° (2°), γ = 84.85° (2°), space group $P\bar{1}$; 7DBN-*p*-Me, triclinic, a = 5.038 (2) Å, b = 5.220 (2) Å, c = 39.057 (2) Å, α = 89.17° (3°), β = 89.75° (4°), γ = 85.01° (4°), space group $P\bar{1}$). The densities, measured by flotation in $ZnCl_2$ solutions, revealed the presence of eight molecules per unit cell in the case of 3DBN-*p*-OMe (d_o = 1.30 g cm^{-3}; d_c = 1.342 g cm^{-3}), one molecule in the case of 5DBN-*p*-Me (d_o = 1.13 g cm^{-3}; d_c = 1.212 g cm^{-3}), and one molecule in the case of 7DBN-*p*-Me (d_o = 1.20 g cm^{-3}; d_c = 1.189 g cm^{-3}). The intensity data collections for all three model compounds were performed on a NONIUS CAD-4 diffractometer with Cu K$\bar{\alpha}$ graphite monochromatized radiation, using the $\omega/2\theta$ scan technique up to a value of 2θ of 140° and at a temperature of −100 °C. The intensities of 3243 independent reflections were thus measured for 3DBN-*p*-OMe, 3521 for 5DBN-*p*-Me, and 3896 for 7DBN-*p*-Me. The reflections for which $I/\sigma(I)$ was greater than 3.00 were declared observed.[6] There were 2177 of these reflections for 3DBN-*p*-OMe (67% of all measured reflections), 2882 for 5DBN-*p*-Me (81%), and 3327 for 7DBN-*p*-Me (85%). In all three cases, the intensities were corrected for polarization and Lorentz effects.[6,9]

The structures were solved by direct methods using the MULTAN80 multisolution program.[7] The atomic coordinates and anisotropic temperature factors for C, N, and O were first refined by full-matrix least squares.[10] The hydrogen atoms of the amide group, the aliphatic chain, the methyl group, and the aromatic ring were then included and refined with isotropic temperature factors. The methyl hydrogens were refined last.

In the case of 5DBN-*p*-Me, one of the two methyl groups was found to be disordered. The two sets of hydrogen atoms corresponding to the two orientations of this methyl group were located by a Fourier difference synthesis. The isotropic temperature factors of these atoms were refined first, while the positions were recalculated after each refinement cycle. The occupation factors were then refined, keeping the temperature factors at fixed values.

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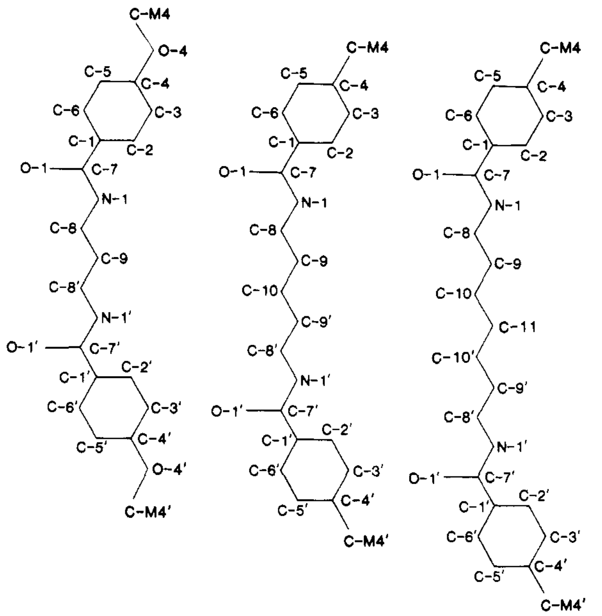

Figure 1. Atomic numbering of the model compounds: (a, left) 3DBN-*p*-OMe, (b, middle) 5DBN-*p*-Me, (c, right) 7DBN-*p*-Me.

The occupation factors converged toward a value of 0.50 for all hydrogen atoms. The values of B_{iso} and of the occupation factors were then kept fixed for the remaining refinement cycles.

Both methyl groups of 7DBN-*p*-Me were found to be disordered. In this case, the SHELX program[8] was used to refine the hydrogen atoms. The positions of the hydrogens were refined first by constraining the geometric variations such as to keep the C–H distances at 0.95 Å, the distances between the hydrogens and the carbon atom C(4) of the aromatic ring at 2.04 Å, and the H–H distances in each methyl group at 1.55 Å. The occupation factors and the isotropic temperature factors were then refined successively. In the last cycles, all the variables related to the methyl hydrogens were held at fixed values.

The final $wR = [\sum w\Delta F^2/\sum wF_o^2]^{1/2}$ was 0.060 for 3DBN-*p*-OMe (0.066 including all reflections), 0.066 for 5DBN-*p*-Me (0.073 including all reflections), and 0.067 for 7DBN-*p*-Me (0.071 including all reflections). The weighting scheme used for 3DBN-*p*-OMe and 5DBN-*p*-Me was $w = 1/[\sigma(I)]^2$. For 7DBN-*p*-Me, a variance analysis was peformed and resulted in the use of a polynomial function of $w = K/\sigma[(I)]^2 + ClF^2$ where Cl is a weighting parameter, which was refined to a final value of 0.0005. At the end of the refinement, the maximum fluctuations of the electron density were –0.34 to 0.29 e Å^{-3} for 3DBN-*p*-OMe, –0.31 to 0.32 e Å^{-3} for 5DBN-*p*-Me, and –0.16 to 0.17 e Å^{-3} for 7DBN-*p*-Me. At that stage, the fluctuations of the atomic coordinates averaged 0.07 for 3DBN-*p*-OMe, 0.02 for 5DBN-*p*-Me, and 0.00 for 7DBN-*p*-Me, while those of the temperature factors averaged 0.05 for 3DBN-*p*-OMe, 0.04 for 5DBN-*p*-Me, and 0.00 for 7DBN-*p*-Me. The scattering factors for C, N, and O atoms were taken from Cromer and Mann[11] and for H atoms from Stewart et al.[12]

The IR spectra were recorded on a FTIR Nicolet 7199 equipped with a He–Ne class II laser. Two hundred scans were accumulated from KBr pellets at a 2-cm^{-1} resolution for each model compound.

The solid-state CP/MAS ^{13}C NMR spectra were taken from a Bruker CXP200 at a frequency of 50.3 MHz, with a DOTY sapphire sample holder rotating at 4 kHz. The spectra were recorded by using the magic angle rotation and cross-polarization and high-power (65-kHz) decoupling, with a contact time of 1 μs and a delay of 10 s between the sequences. An average of 700 scans was used for all model compounds. All spectra were recorded at room temperature.

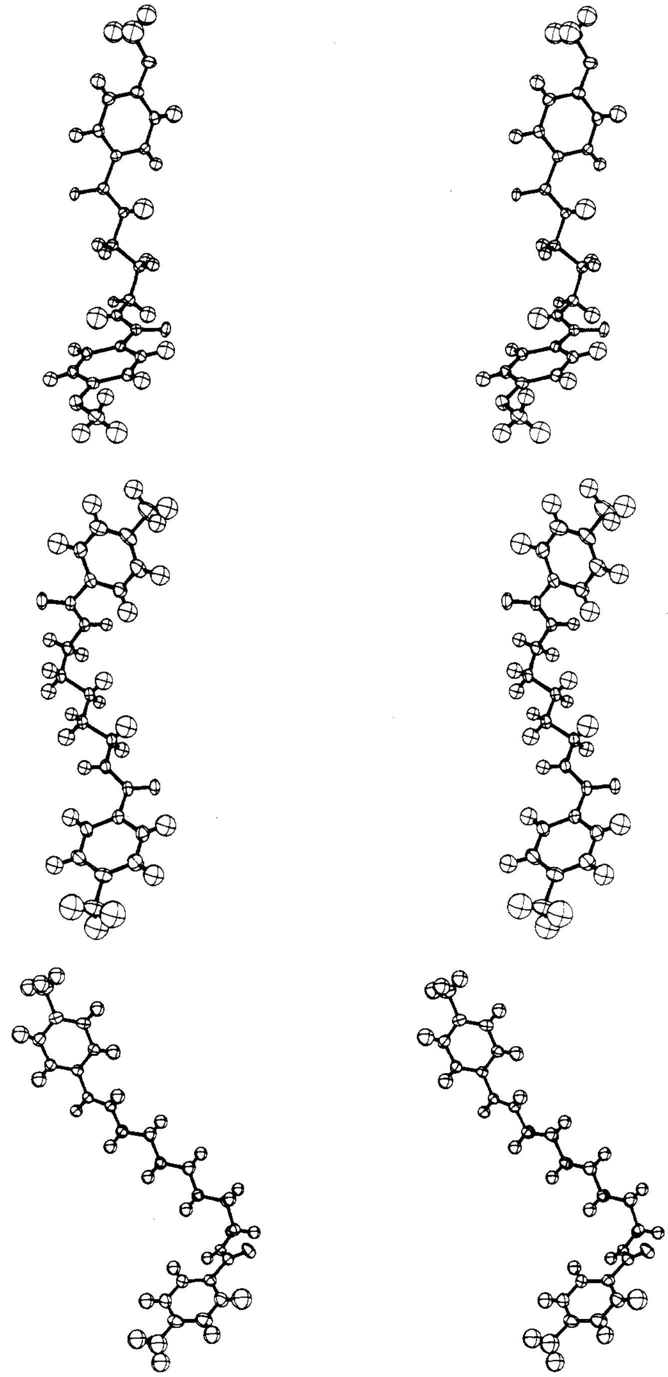

Figure 2. Stereoscopic views of the molecules: (a, top) 3DBN-*p*-OMe, (b, middle) 5DBN-*p*-Me, (c, bottom) 7DBN-*p*-Me.

Results and Discussion

Crystal Structures of Model Compounds. The atomic numbering adopted for each model compound is shown in Figure 1. Primed symbols refer to chemically equivalent atoms. Stereoscopic views[13] of the molecules appear in Figure 2, and the lists of the final atomic coordinates are given in Table I. In Table II are compared the bond distances, bond angles, and torsion angles of the three compounds. These are in good agreement with the corresponding quantities reported for the other model compounds.[2-4,14-16]

Molecular Conformation. The torsion angles describing the methylenic sequence of atoms indicate that all three model compounds have similar conformation. The first torsion angle, τ = C(7)–N(1)–C(8)–C(9), is always near 90°, while the last torsion angle of the sequence, τ' = C(7′)–N(1′)–C(8′)–C(9′), is always near 180°. In between τ and τ', one always finds a segment in the gt conformation followed by an all-trans section (t = trans, g = gauche). It is this trans section that increases in length as one goes from 3DBN-*p*-OMe to 5DBN-*p*-Me and to 7DBN-*p*-Me. Interestingly, this conformation differs from

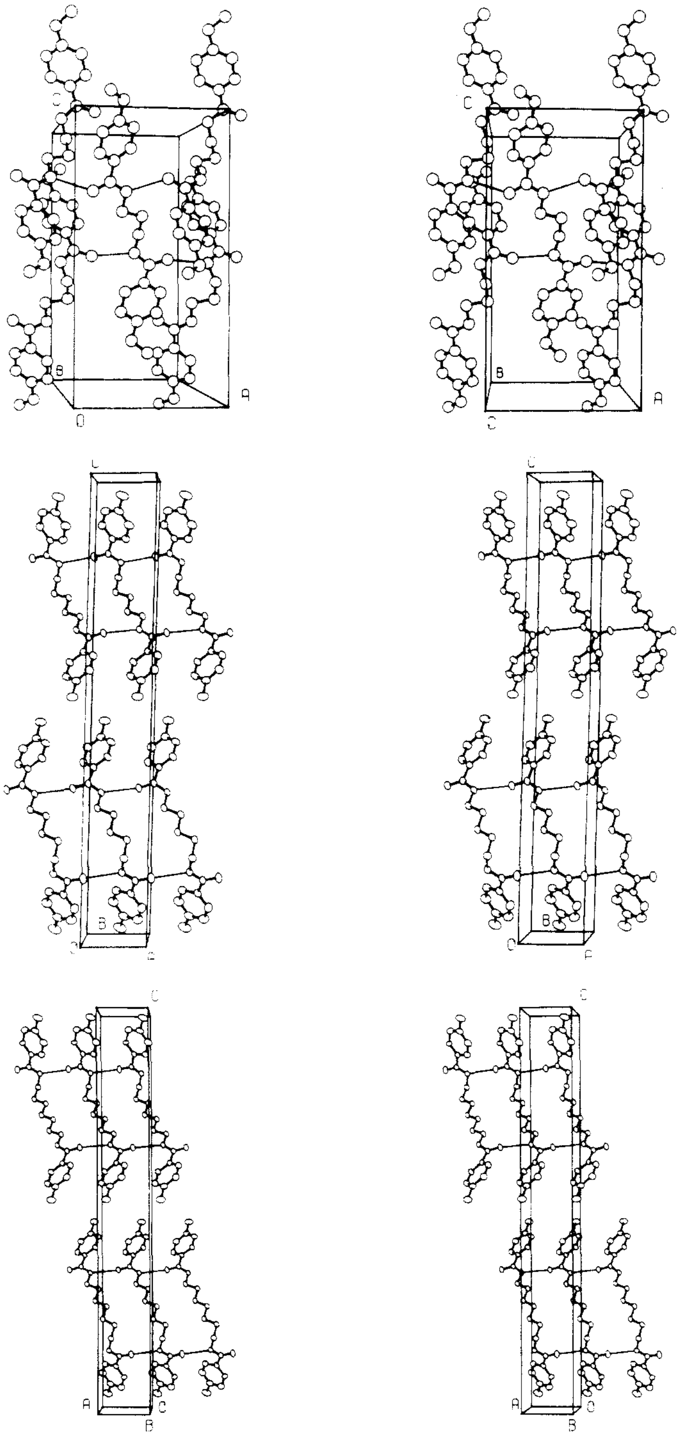

Figure 3. Stereoscopic views of the packings: (a, top) 3DBN-*p*-OMe, (b, middle) 5DBN*p*-Me, (c, bottom) 7DBN-*p*-Me.

those reported for the unsubstituted model compounds. In 5DBN[1] and 7DBN,[16] both τ and τ' have values close to 90°. The situation of 3DBN[1] with $\tau = 87.4°$ (3°) and $\tau' = -140.3°$ (3°) is about half-way between that of 5DBN (or 7DBN) and that of the model compounds described here. In the case of the even *n*DBN (n = 4, 6, 8, and 10),[14,15,17] $\tau = \tau' \approx 180°$, while for 2DBN[4] $\tau = \tau' \approx 90°$. Thus, with only one exception, whether the *n*DBN's are substituted or not, τ and τ' may be all near 90, or all near 180°, or with $\tau \approx 90°$ and $\tau' \approx 180°$.

The values of two important dihedral angles are reported in Table III. The angle, ϵ, between the aromatic ring and the amide group has values in the vicinity of 30° ± 2°. This is in agreement with the observations made for all the other *n*DBN's. There is, however, one exception, that of 3DBN-*p*-OMe for which $\epsilon = 14.6°$ and $\epsilon' = 20.1°$. A value of $\epsilon = 19°$ was observed for 2DBN.[4] This marked difference is associated with the packing mode adopted by this compound (see below).

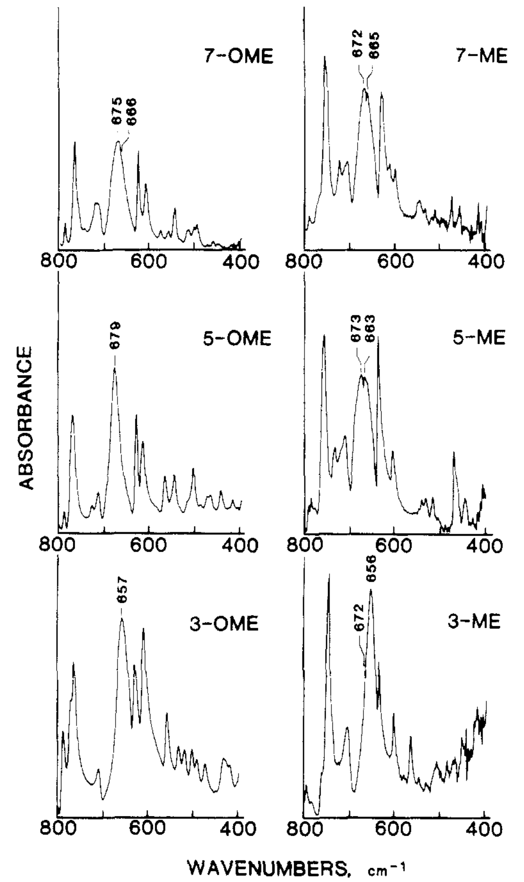

Figure 4. Region of the amide V band in IR spectroscopy.

Packing and H Bonding. The molecular packings are shown in Figure 3. We can observe that although 3DBN-*p*-OMe, 5DBN-*p*-Me, and 7DBN-*p*-Me have comparable conformations their molecular organizations do differ significantly. In the case of 5DBN-*p*-Me and 7DBN-*p*-Me, each molecule is linked to only two others by hydrogen bonds, forming pleated ribbons, extending parallel to the *a* axis (n = 5) or the *b* axis (n = 7). This type of packing is the most frequently observed for *n*DBN's (n = 4, 6–10). However, in the case of 3DBN-*p*-OMe, each molecule is hydrogen bonded to four neighboring molecules, forming sheets of hydrogen-bonded molecules. This packing is very similar to that reported for 2DBN.[4] It must be the rather bulky substituent and the short methylenic sequence which forces the adoption of such a packing mode. The geometrical characteristics of the hydrogen bonding of the model compounds are compared in Table IV.

IR Spectroscopy of Model Compounds. Previous studies of model compounds have shown that the position of the amide V band, δ(N–H) or out-of-plane vibration, was related to the values of the τ torsion angles.[3] When $\tau \approx 180°$, it was found to be 652–660 cm^{-1} and when $\tau \approx 90°$, it was near 670 cm^{-1}. In the present case, the two τ angles in each molecule are very different from one another. Thus, we expected two absorptions, one in the vicinity of 670 cm^{-1} corresponding to $\tau \approx 90°$ and the other around 660 cm^{-1} associated with $\tau \approx 180°$. The amide V region of the infrared spectra of *n*-DBN-*p*-Me and *n*-DBN-*p*-OMe with n = 3, 5, 7 is shown in Figure 4. In the case of 5DBN-*p*-Me and 7DBN-*p*-Me, the amide V band is very

Table I
Final Atomic Coordinates (×10^5) and U_{eq} (×10^4) for (a) 3DBN-*p*-OMe, (b) 5DBN-*p*-Me (At. Coord ×10^4), and (c) 7DBN-*p*-Me

atom	X	Y	Z	U_{eq}	atom	X	Y	Z	U_{eq}
(a) 3DBN-*p*-OMe									
O(1)	66 858 (21)	22 040 (13)	49 595 (12)	337	O(1′)	14 642 (21)	14 484 (13)	72 675 (11)	329
O(C)	38 880 (22)	8 784 (12)	21 954 (11)	294	O(C′)	30 852 (25)	48 (13)	102 398 (12)	376
N(1)	45 357 (25)	25 596 (15)	51 585 (13)	235	N(1′)	36 961 (25)	16 943 (14)	72 743 (13)	260
C(1)	50 145 (31)	18 360 (17)	41 116 (15)	224	C(1′)	27 388 (31)	10 247 (16)	82 689 (16)	229
C(2)	37 525 (30)	19 650 (16)	37 881 (16)	230	C(2′)	38 366 (31)	11 483 (17)	87 342 (16)	238
C(3)	34 142 (31)	16 365 (17)	31 589 (16)	242	C(3′)	38 998 (32)	7 991 (17)	93 813 (16)	265
C(4)	43 164 (32)	11 598 (16)	28 293 (16)	233	C(4′)	29 058 (34)	3 131 (17)	95 870 (17)	280
C(5)	55 611 (32)	10 128 (17)	31 491 (16)	258	C(5′)	18 186 (36)	1 860 (19)	91 323 (18)	333
C(6)	58 996 (31)	13 552 (18)	37 841 (16)	259	C(6′)	17 441 (33)	5 426 (19)	84 882 (17)	300
C(7)	54 747 (32)	22 131 (17)	47 727 (16)	245	C(7′)	25 849 (33)	13 984 (17)	75 717 (16)	246
C(8)	48 839 (33)	29 556 (17)	58 059 (16)	260	C(8′)	35 932 (33)	21 411 (18)	66 425 (16)	270
C(9)	49 644 (31)	24 697 (18)	64 602 (16)	252	C(M4′)	21 566 (46)	−5 366 (22)	104 568 (21)	530
C(M4)	47 914 (37)	4 014 (18)	18 253 (17)	344					
(b) 5DBN-*p*-Me									
O(1)	−766 (4)	5 793 (4)	−1 579 (1)	483	O(1′)	11 726 (3)	−1 138 (3)	−3 345 (1)	356
N(1)	3 591 (4)	6 112 (4)	−1 708 (1)	302	N(1′)	7 328 (4)	52 (4)	−3 265 (1)	313
C(1)	2 356 (5)	3 198 (5)	−1 207 (1)	328	C(1′)	8 848 (5)	−2 923 (4)	−3 762 (1)	295
C(2)	4 671 (6)	1 509 (5)	−1 232 (1)	387	C(2′)	6 693 (5)	−2 284 (5)	−3 989 (1)	395
C(3)	5 219 (6)	−366 (5)	−950 (1)	495	C(3′)	6 336 (6)	−3 725 (6)	−4 298 (1)	440
C(4)	3 581 (6)	−576 (5)	−642 (1)	463	C(4′)	8 071 (6)	−5 891 (5)	−4 387 (1)	405
C(5)	1 300 (7)	1 128 (6)	−618 (1)	570	C(5′)	10 193 (6)	−6 547 (5)	−4 155 (1)	441
C(6)	697 (6)	2 982 (6)	−901 (1)	498	C(6′)	10 597 (5)	−5 096 (5)	−3 848 (1)	377
C(7)	1 611 (5)	5 165 (5)	−1 515 (1)	323	C(7′)	9 406 (5)	−1 323 (4)	−3 438 (1)	295
C(8)	3 109 (5)	7 898 (5)	−2 032 (1)	342	C(8′)	7 697 (5)	1 688 (5)	−2 960 (1)	319
C(9)	2 856 (5)	6 390 (5)	−2 384 (1)	310	C(9′)	5 115 (5)	3 208 (5)	−2 845 (1)	310
C(10)	5 443 (5)	4 876 (4)	−2 511 (1)	293	C(M4′)	7 682 (7)	−7 448 (6)	−4 727 (1)	602
C(M4)	4 222 (8)	−2 635 (6)	−340 (1)	700					
(c) 7DBN-*p*-OMe									
O(1)	60 429 (22)	−53 126 (26)	−14 313 (3)	490	O(1′)	−72 953 (21)	56 352 (23)	−34 952 (3)	391
N(1)	17 039 (27)	−55 304 (25)	−15 564 (3)	335	N(1′)	−29 248 (25)	44 637 (26)	−34 228 (3)	331
C(1)	28 415 (31)	−27 954 (31)	−10 979 (4)	349	C(1′)	−42 902 (29)	75 268 (29)	−38 742 (4)	316
C(2)	44 495 (39)	−26 731 (42)	−8 125 (5)	508	C(2′)	−59 872 (35)	97 014 (33)	−39 508 (5)	399
C(3)	37 721 (45)	−9 210 (45)	−5 585 (5)	567	C(3′)	−54 736 (40)	112 742 (36)	−42 285 (5)	463
C(4)	15 288 (43)	7 774 (35)	−5 825 (5)	492	C(4′)	−33 053 (38)	106 815 (34)	−44 420 (4)	426
C(5)	−564 (45)	6 686 (35)	−8 704 (5)	509	C(5′)	−16 130 (38)	85 049 (38)	−43 635 (4)	452
C(6)	5 719 (37)	−11 035 (32)	−11 240 (5)	414	C(6′)	−20 717 (34)	69 476 (35)	−40 821 (4)	397
C(7)	36 651 (30)	−46 555 (31)	−13 745 (4)	346	C(7′)	−49 617 (29)	58 142 (29)	−35 817 (4)	311
C(8)	22 658 (34)	−72 274 (31)	−18 449 (4)	357	C(8′)	−34 331 (30)	26 716 (32)	−31 447 (4)	336
C(9)	28 034 (31)	−57 105 (31)	−21 713 (4)	339	C(9′)	−9 317 (29)	10 605 (30)	−30 343 (4)	323
C(10)	3 656 (30)	−40 618 (30)	−23 026 (4)	320	C(10′)	−14 997 (30)	−7 211 (30)	−27 369 (4)	325
C(11)	9 551 (30)	−23 503 (30)	−26 069 (4)	326	C(M4′)	−27 938 (49)	123 392 (42)	−47 504 (5)	595
C(M4)	8 081 (56)	27 299 (43)	−3 097 (6)	691					

wide but clearly split in two components, in agreement with the crystal structure results. However, we observe only one wide band for 3DBN-*p*-OMe, although it has τ angles comparable to those of the above two model compounds.

Conformational Analysis. The conformational analyses of 3T nylon and 5T nylon were presented in the first article of this series.[1] However, in these early calculations, we had not considered the situations where $\tau \approx 180°$ and $\tau' \approx 90°$ since no model compound had shown this type of conformation. We now feel that it is important to include this case in our analysis. The results of these new conformational energy calculations, performed by using the CRYSP program,[18] as well as the calculated fiber repeats, p_c, associated to each energy minimum, are given in Table V. The reader is referred to our previous paper for the procedural details.[1] The new minima are assigned the subscript "T" to distinguish them from those with $\tau \approx \tau'$.

The conformation V_T of 3T nylon associated with one of the new minima qualitatively corresponds to that found in the crystal structure of 3DBN-*p*-OMe. However, this calculated conformation deviates significantly from the observed one, particularly at the τ angle which is −153.3° for minimum V_T but −177.2° (3°) in 3DBN-*p*-OMe. Such a deviation is attributed in part to the aromaticity of the benzamido group which is amplified by the presence of the methoxy substituent on the aromatic ring. It should be noted that the influence of the aromaticity on the conformation is not taken into account by the calculation method used. For comparison purpose, the τ angle of interest has a value of −140.3° (3°) in 3DBN.

The calculated fiber repeat of 20.2 Å for the minimum V_T of 3T nylon is far from the experimentally observed value for 3T nylon, p_o = 21.40 Å, and from the corresponding distance of 20.984 (4) Å in 3DBP-*p*-OMe. The latter is twice the distance between the aromatic ring centers in 3DBN-*p*-OMe. Of the remaining conformational minima, only conformations II_T and possibly IV_T allow for values of the calculated fiber repeat, p_c, close to the observed one (21.2 and 20.6 Å, respectively, versus p_o = 21.40 Å for 3T nylon). Conformations II_T and IV_T differ from one another by an interchange of the values of ϕ_1 and ϕ_1' and a slightly more open τ' torsion angle in IV_T.

Similarly, for 5T nylon, one conformational minimum, IV_T, corresponds to the conformation of 5DBN-*p*-Me. The experimental value of the fiber repeat of this polyamide, p_o = 26.4 Å, is very different from that calculated for 5DBN-*p*-Me (p_c = 23.91 Å) or from the conformation associated with minimum IV_T (24.82 Å). This conformation can thus be ruled out. Among the new minima calculated for 5DBN-*p*-Me, only minimum I_T leads to a calculated

Table II
Bond Distances (Å), Bond Angles, and Torsion Angles (deg) of the Three Model Compounds[a]

		3DBN-*p*-OMe		5DBN-*p*-Me		7DBN-*p*-Me	
		(1)	(2)	(1)	(2)	(1)	(2)
		The Benzamide Moiety					
	C(1)–C(2)	1.403 (4)	1.407 (4)	1.395 (4)	1.391 (4)	1.386 (2)	1.393 (2)
	C(2)–C(3)	1.390 (4)	1.389 (4)	1.391 (4)	1.379 (4)	1.382 (2)	1.393 (2)
	C(3)–C(4)	1.367 (4)	1.375 (4)	1.368 (4)	1.391 (4)	1.387 (2)	1.391 (2)
	C(4)–C(5)	1.388 (4)	1.377 (4)	1.385 (4)	1.390 (4)	1.377 (3)	1.388 (2)
	C(5)–C(6)	1.397 (4)	1.386 (4)	1.391 (4)	1.381 (4)	1.381 (3)	1.388 (2)
	C(6)–C(1)	1.391 (4)	1.361 (4)	1.369 (4)	1.395 (4)	1.386 (3)	1.390 (2)
	C(1)–C(7)	1.492 (4)	1.485 (4)	1.507 (4)	1.494 (4)	1.496 (2)	1.496 (2)
	O(1)–C(7)	1.243 (4)	1.245 (4)	1.243 (3)	1.242 (3)	1.237 (2)	1.233 (2)
	N(1)–C(7)	1.338 (4)	1.345 (4)	1.319 (3)	1.333 (3)	1.336 (2)	1.342 (2)
	C(4)–O(C) or C(4)–C(M4)	1.363 (4)	1.361 (4)	1.511 (4)	1.508 (4)	1.507 (3)	1.507 (3)
	O(C)–C(M4)	1.433 (4)	1.418 (4)				
	C(1)–C(2)–C(3)	120.8 (3)	120.2 (3)	119.5 (3)	120.7 (3)	120.4 (2)	120.0 (2)
	C(2)–C(3)–C(4)	121.4 (3)	122.1 (3)	122.0 (3)	121.3 (3)	121.2 (2)	121.5 (2)
	C(3)–C(4)–C(5)	120.5 (3)	121.3 (3)	118.0 (3)	117.8 (3)	117.9 (2)	118.0 (2)
	C(4)–C(5)–C(6)	119.3 (3)	119.7 (3)	120.7 (3)	121.6 (3)	121.5 (2)	121.0 (2)
	C(5)–C(6)–C(1)	119.6 (3)	119.0 (3)	121.0 (3)	120.2 (3)	120.4 (2)	120.6 (2)
	C(6)–C(1)–C(2)	118.3 (3)	117.7 (3)	118.7 (3)	118.6 (3)	118.6 (2)	118.8 (2)
	C(2)–C(1)–C(7)	123.1 (3)	123.2 (3)	121.3 (2)	122.5 (2)	122.1 (2)	121.9 (2)
	C(6)–C(1)–C(7)	119.3 (3)	118.5 (3)	119.9 (2)	119.9 (2)	119.3 (2)	119.2 (2)
	C(1)–C(7)–O(1)	121.8 (3)	121.2 (3)	120.1 (2)	120.6 (2)	121.2 (2)	121.0 (2)
	C(1)–C(7)–N(1)	118.1 (3)	117.6 (3)	116.5 (2)	117.1 (2)	116.4 (2)	117.2 (2)
	O(1)–C(7)–N(1)	120.1 (3)	121.3 (3)	123.4 (2)	122.2 (2)	122.4 (2)	121.8 (2)
	C(3)–C(4)–O(C)	115.5 (3)	115.6 (3)				
	C(5)–C(4)–O(C)	124.9 (3)	125.4 (3)				
	C(3)–C(4)–C(M4)			120.9 (3)	121.0 (3)	120.3 (2)	120.8 (2)
	C(5)–C(4)–C(M4)			121.1 (3)	121.2 (3)	121.8 (2)	121.2 (2)
	C(4)–O(C)–C(M4)	117.7 (2)	118.1 (3)				
		The Methylenic Sequence					
	N(1)–C(8)	1.458 (4)	1.448 (4)	1.470 (3)	1.462 (3)	1.455 (2)	1.460 (2)
	C(8)–C(9)	1.523 (4)	1.520 (4)	1.518 (4)	1.512 (3)	1.527 (2)	1.514 (2)
	C(9)–C(10)			1.525 (3)	1.518 (3)	1.523 (2)	1.519 (2)
	C(10)–C(11)					1.520 (2)	1.523 (2)
	N(1)–C(8)–C(9)	112.5 (3)	110.5 (3)	111.2 (2)	111.5 (2)	111.4 (1)	112.2 (1)
	C(8)–C(9)–C(8′)	111.8 (3)					
	C(8)–C(9)–C(10)			113.4 (2)	111.8 (2)	113.4 (1)	111.1 (1)
	C(9)–C(10)–C(9′)			112.9 (2)			
	C(9)–C(10)–C(11)					113.8 (1)	113.8 (1)
	C(10)–C(11)–C(10′)					113.0 (1)	
	C(2)–C(1)–C(7)–O(1)	−164.6 (5)	−158.8 (5)	148.0 (4)	−147.9 (4)	148.0 (2)	−148.5 (2)
	C(2)–C(1)–C(7)–N(1)	15.6 (5)	20.4 (5)	−31.2 (3)	29.9 (3)	−31.3 (2)	30.5 (2)
	C(6)–C(1)–C(7)–O(1)	12.7 (5)	19.5 (5)	−29.7 (3)	30.1 (3)	−29.1 (2)	28.6 (2)
	C(6)–C(1)–C(7)–N(1)	−167.0 (4)	−161.3 (4)	151.1 (3)	−152.2 (3)	151.6 (2)	−152.4 (2)
τ, τ'	C(7)–N(1)–C(8)–C(9)	−83.5 (4)	174.2 (3)	−85.7 (3)	171.7 (2)	−83.5 (2)	171.6 (1)
ϕ, ϕ_1'	N(1)–C(8)–C(9)–C(8′)	−64.7 (3)	−178.8 (3)				
ϕ_1, ϕ_1	N(1)–C(8)–C(9)–C(10)			−67.8 (3)	176.0 (2)	−67.0 (2)	178.1 (1)
ϕ_2, ϕ_2'	C(8)–C(9)–C(10)–C(9′)			175.5 (2)	−178.9 (2)		
ϕ_2, ϕ_2'	C(8)–C(9)–C(10)–C(11)					174.3 (1)	−178.5 (1)
ϕ_3, ϕ_3'	C(9)–C(10)–C(11)–C(10′)					179.7 (1)	178.3 (1)

[a] (1) Primed atoms; (2) unprimed atoms.

Table III
Dihedral Angles (deg) of Interest[a]

	3DNB-*p*-OMe		5DBN-*p*-Me		7DBN-*p*-Me	
	(1)	(2)	(1)	(2)	(1)	(2)
aromatic ring/amide group	14.6	20.1	31.0	31.5	30.6	30.1
amide group/plane of methylene groups	107.5	6.8	104.0	9.1	101.7	7.4

[a] (1) Unprimed atoms; (2) primed atoms.

value of the fiber repeat, $p_c = 26.8$ Å, approaching that of 5T nylon ($p_o = 26.4$ Å). However, if we keep in mind the fact that the fiber diagrams of *n*T nylons with *n* odd are very similar to one another and that there is a regular incrementation of the fiber repeat of these polyamides as *n* increases, the conformations proposed must be similar for $n = 3$, 5, and 7. This is not the case for minimum $\mathrm{III_T}$ of 3T nylon and minimum $\mathrm{I_T}$ of 5T nylon.

We are left to propose that, as was previously suggested, the chain conformations must be one of the two shown below:

	I	II
3T nylon	$\tau^-\mathrm{tg}^+\tau^+$	$\tau^+\mathrm{tg}^-\tau^+$
5T nylon	$\tau^-\mathrm{tttg}^+\tau^+$	$\tau^+\mathrm{tg}^-\mathrm{tt}\tau^+$

Until now, we have not discussed the structure of 7T nylon. Statton,[19] who first published the fiber diagram of 7T nylon, proposed an all-trans conformation, without giving the value of the observed fiber repeat. We have recently obtained a fiber diagram of this polyamide of average orientation. It seems to be of a slightly better quality than that of Statton. This fiber diagram shows strong similarities with those of the 3T and 5T nylons (Figure 5). The fiber repeat obtained by indexing the most intense meridional reflection spot as 002, as was the case for 3T nylon and 5T nylon, leads to an observed value of 31.4 Å. Interestingly, we note a progression of ~5 Å when passing from $n = 3$ to $n = 5$, and again from $n = 5$ to $n = 7$. This increment is twice that of the advance of

Table IV
Characteristics of the Hydrogen Bonds

	N-H, Å	H···O*, Å	N···O*, Å	N-H···O*, deg	H···O*-C*, deg
		3DBN-*p*-OMe			
N(1)-H(N1)···O(1*)	0.85 (4)	2.04 (4)	2.849 (3)	159 (4)	157.1 (2)
N(1′)-H(N1′)···O(1′*)	0.86 (4)	2.04 (4)	2.893 (3)	172 (4)	135.3 (2)
		5DBN-*p*-Me			
N(1)-H(N1)···O(1*)	0.98 (2)	1.93 (2)	2.894 (3)	167 (2)	168.2 (2)
N(1′)-H(N1′)···O(1′*)	1.01 (2)	1.97 (2)	2.960 (3)	165 (2)	168.4 (2)
		7DBN-*p*-Me			
N(1)-H(N1)···O(1*)	0.92 (2)	1.99 (2)	2.884 (2)	165 (2)	166.2 (2)
N(1′)-H(N1′)···O(1′*)	0.92 (2)	2.06 (2)	2.964 (2)	170 (2)	167.2 (2)

Table V
Results of the Conformational Analysis of 3T Nylon and 5T Nylon ($\tau \approx 180°$, $\tau' \approx 90°$) and Comparison with the Corresponding Torsion Angles Observed in the Model Compounds

	E^a	τ', deg	ϕ_1', deg	ϕ_1, deg	τ, deg	p_c, Å
			3T Nylon			
conformational anal.						
I_T	0.0	172.5	171.1	170.1	170.2	23.6
II_T	II_T	97.4	170.0	70.0	−150.6	21.2
III_T	4.0	97.8	−170.0	−70.0	179.4	22.4
IV_T	4.0	114.8	−70.0	−170.0	−147.2	20.6
V_T	5.0	91.7	69.0	−170.4	−153.3	20.2
model compds						
3DBN		87.4 (3)	64.1 (3)	176.1 (2)	−140.3 (3)	21.406 (7)
3DBN-*p*-OMe		83.5 (4)	64.7 (3)	175.8 (3)	−177.2 (3)	20.984 (4)

	E^a	τ, deg	ϕ_1, deg	ϕ_2, deg	ϕ_2', deg	ϕ_1', deg	τ', deg	p_c, Å
				5T Nylon				
conformational anal.								
I_T	0.0	93.0	180	180	180	76.7	180	26.78
II_T	0.9	94.2	180	180	180	−66.7	180	27.40
III_T	1.5	107.0	−68	180	180	180	180	24.18
IV_T	2.1	87.2	65.6	180	180	180	180	24.82
V_T	3.3	97.6	180	75.3	180	180	180	27.20
VI_T	3.7	93.7	180	−76	180	180	180	28.40
VII_T	7.4	93.7	180	180	−81.8	180	180	24.92
$VIII_T$	8.3	93.5	180	180	77.3	180	180	25.60
model compds								
5DBN		90.2 (2)	165.3 (2)	59.6 (2)	176.8 (2)	55.8 (2)	71.3 (2)	23.770 (3)
5DBN-*p*-Me		85.7 (3)	67.8 (3)	−175.5 (2)	178.9 (2)	−176.0 (2)	−171.7 (2)	23.908 (4)

[a] Conformational energy in arbitrary units. The values are given relative to the lowest energy which is set at 0.0.

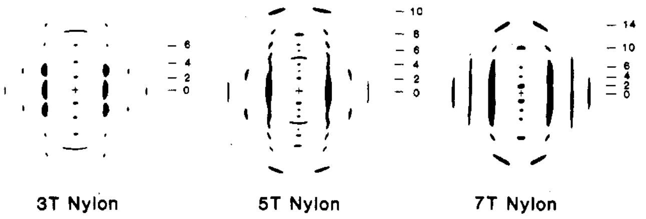

Figure 5. Schematic representation of the X-ray fiber patterns of 3T, 5T, and 7T nylons.

a methylene group in the trans conformation. Thus, it is proposed that the conformation of 7T nylon is similar to those of 3T nylon and 5T nylon, namely, that it should be either I τ^{-}tttttg$^{+}\tau^{+}$ or II τ^{+}tg^{-}ttttτ^{+}.

In all cases, the possibility of an all-trans conformation is entirely ruled out, since for a chain of 7T nylon in the all-trans conformation p_c = 34.2 Å, a value which is clearly higher than the observed fiber repeat of 31.4 Å. The equivalent fiber repeats calculated from the crystal structures of 7DBN and 7DBN-*p*-Me are 33.578 (9) Å and 28.304 (2) Å, respectively. Thus, the conformations of these model compounds have no relation to that of 7T nylon.

Solid-State ^{13}C CP/MAS NMR Spectroscopy. The following analysis of the ^{13}C CP/MAS NMR spectra of the model compounds and of the *n*T nylons is largely dependent on a previous study of various model compounds of 4T nylon[2] and of models of poly(tetramethyleneterephthalate).[20] In the former study, two main effects were recognized: Firstly, the value of the C(7)–N(1)–C(8)–C(9) torsion angle, or τ, was related to a "pseudo"-γ-gauche effect. This effect is downfield instead of being upfield, the usual direction of the γ-gauche effect. This has been tentatively attributed to an interaction between C(9) and the electron cloud of the amide group, which has a deshielding effect. The magnitude of the pseudo-γ-gauche effect is 2 ± 1 ppm. Secondly, atom C(8) may also be influenced by the type of packing of the molecules. This is due in part to van der Waals interactions between atoms, but there is also an important contribution from the influence of the electron cloud of aromatic rings of adjacent molecules.

In Figure 6 are presented the solid-state ^{13}C NMR spectra of the polymers and of their model compounds, while in Table VI are listed the corresponding chemical shifts. The torsion angles which could induce a γ-gauche effect on the chemical shifts of the various carbon atoms are identified in Figure 7. It should be noted that the C(7) and C(8) signals usually appear as doublets. This is due to the anisotropy of the nitrogen atom to which they are bonded.

Model Compounds. The chemical shift of C(9) in 3DBN is +2.9 ppm downfield from that of 3DBN-*p*-OMe. This agrees well with the fact that 3DBN has both τ and τ' near 90°, whereas in 3DBN-*p*-OMe one of these torsion

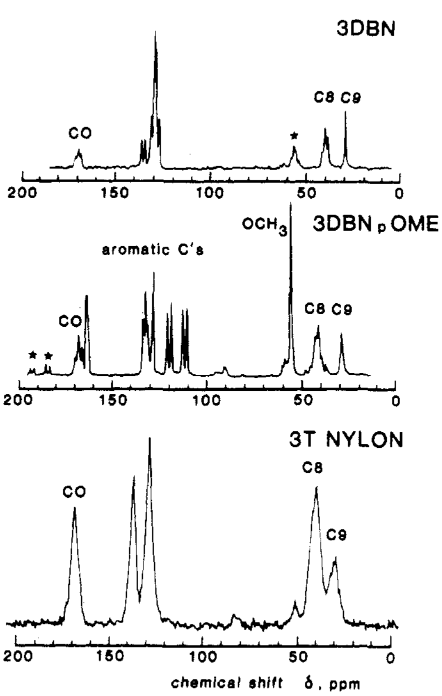

Figure 6. Solid-state CP/MAS ^{13}C NMR spectra of 3T nylon and of its model compounds. The stars refer to the spinning side bands.

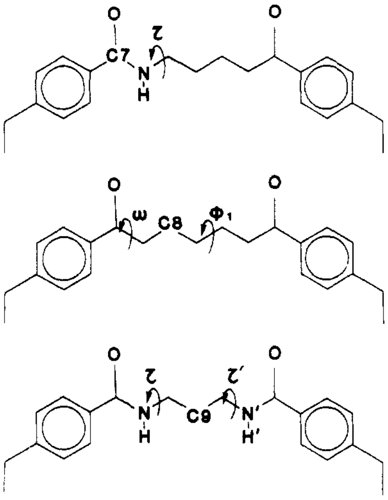

Figure 7. Possible γ-gauche effects on the C atoms of 3T nylon and of its model compounds.

angles is near 90° while the other is near 180°.

Atom C(8) may be influenced by the ω and ϕ_1 torsion angles, as well as by possible interchain interactions. Similarly atom C(8′) may be influenced by the corresponding primed torsion angles. Both molecular packings offer possibilities of interactions between C(8) and the electron cloud of the aromatic ring of neighboring molecules. Since the ω torsion angle is always observed close to 180°, only ϕ_1 and ϕ_1' need to be taken into account. A previous analysis of the model compounds of 4T nylon has enabled us to evaluate the γ-gauche effect of these torsion angles at about 2 ppm. Since for both model compounds 3DBN and 3DBN-p-OMe $\phi_1 \approx 180°$ and $\phi_1' \approx 60°$, C(8) and C(8′) should have the same chemical shifts in both compounds. However, there is a deviation of 0.4 ppm for C(8′) and of 1 ppm for C(8). These deviations may be attributed to differences in the interchain interactions. The difference of the mean chemical shifts of both doublets is −2.0 ppm for 3DBN and −1.4 ppm for 3DBN-p-OMe. These quantities are slightly smaller than those reported for the benzoates (−3 ppm).[20] This might be due to the presence of the nitrogen atom instead of the oxygen atom of the benzoates.

Table VI
Chemical Shifts (δ, ppm) of 3T Nylon and of Its Model Compounds

	3T nylon		3DBN		3DBN-p-OMe	
C(9)	28.1		29.5		26.6	
	28.4					
	28.9					
	30.1					
		mean		mean		
C(8)			42.3			
	40.9		40.9	41.6	40.6	
C(8′)	40.1		40.0		39.2	
	39.2	39.6	39.2	39.6		
C(1)	137.8		137.7		126.6	
C(1′)						
C(2)			130.5		132.1	
C(2′)					130.6	
C(3)			129.4		110.8	
C(3′)	129.6				108.5	
C(4)	129.1		129.7		162.7	
C(4′)	128.0				161.9	
C(5)			129.4		119.1	
C(5′)					116.8	
C(6)			129.4		130.6	
C(6′)					129.3	
		mean		mean		mean
C(7)	170.5		170.4		166.9	
	168.2	169.4	168.2	169.3	164.9	165.9
C(7′)	166.2		169.0		168.6	
			167.5	168.3	166.9	167.8
CH_3					54.2	

The last carbon atoms to be analyzed with respect to the γ-gauche effect are those of the amide group, C(7) and C(7′). They can only be affected by the values of τ and τ', respectively. Both of these torsion angles are relatively close to one another for the former compound but are quite different for the latter. For 3DBN, there is a difference of only 1.0 ppm between the two doublets, but this difference is 1.9 ppm for 3DBN-p-OMe. The two values of 3DBN are relatively close to one of the values of 3DBN-p-OMe (169.3 and 168.3 ppm for 3DBN compared to 167.8 ppm). We therefore assigned this latter doublet to the carbon atom affected by the same pseudo-γ-gauche effect as for the two carbon atoms of 3DBN, namely, C(7′). The value of this pseudo-γ-gauche effect is thus approximately +2 ppm and is related to the value of the τ or τ' torsion angle. It must be noted that the assignment of the C(7) and C(7′) atoms is tentative and might be interchanged because of the similarity of the effects encountered.

3T Nylon. In the case of 3T nylon, the peaks are not very well resolved. This is largely due to the poor crystallinity of the sample. This polyamide is very difficult to obtain in a highly crystalline form. The two possible conformations which have been previously proposed differ only by the signs of the torsion angles. Consequently, for 3T nylon, the ^{13}C solid-state NMR spectroscopy does not allow us to distinguish between these two conformations. We have included in Table VII a comparison of the position of the peaks with those expected for different conformations from the study of the model compounds. The C(8) region gives information on the ϕ_1 and ϕ_1' torsion angles. This region is also susceptible to variations due to interchain interactions. In this case, however, the observed values agree well with those of the conformational analysis, since they encompass the region of 39.2 ppm for $\phi_1 \approx 60°$ to 40.1–40.9 ppm for $\phi_1 \approx 180°$.

In the case of the C(7′) signals, we observe peaks ranging from 166.2 to 170.5 ppm which includes the regions of τ

Table VII
Observed Chemical Shifts of 3T Nylon As Compared to Those Predicted for Various Conformations

	torsion angle values	δ_{pred},[a] ppm	δ_{obsd},[a] ppm
C(9)			28.1
	$\tau \approx \tau' \approx 90°$	29.5	28.4
	$\tau \approx 90°$, $\tau' \approx 180°$	26.6	28.9
	$\tau \approx \tau' \approx 180°$	23.6	30.1
C(8) or C(8′)	ϕ_1 or $\phi_1' \approx 60°$	39.2–39.6	39.2
			40.1
	ϕ_1 or $\phi_1' \approx 180°$	40.6–41.6	40.9
C(7)	$\tau \approx 90°$	167.8–169.3	170.5
			168.2
	$\tau \approx 180°$	165.9	166.2

[a] Values predicted from model compounds of known conformations.

$\approx 180°$ (165.9 ppm) and of $\tau \approx 90°$ (167.8–167.9 ppm). Since the chemical shifts of C(7) and C(7′) are much more affected by interchain interactions than that of C(9), we will use only the C(9) signal to deduce the value of τ. For atom C(9), we observe a broad peak from 28.1 to 30.1 ppm. This region corresponds to values of τ and τ' near 90° in the case of the model compounds. This observation is in agreement with the conformational analysis calculations.

It must nevertheless be emphasized that this analysis is subject to revision should a spectrum of a more crystalline sample of the polyamide be obtained. In summary, the peak assigned to C(8) and C(8′) is large enough to indicate that both values of ϕ are present in the polyamide. Furthermore, the broad C(9) signal confirms a τ value of 90°. It is satisfying that both of these assignments correspond to the conformations arrived at by conformational analysis.

Conclusion

In this second article we have implemented the use of ^{13}C CP/MAS solid-state NMR spectroscopy. We have shown that, even on samples of medium crystallinity, we could arrive at an interpretation which is consistent with that derived from IR spectroscopy, X-ray diffraction, and conformational analysis. However, it must be realized that many factors influence the chemical shifts of the carbon atoms, and thus a study of the model compounds is imperative at this stage of the development of the method.

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Registry No. 3DBN-*p*-OMe, 118018-55-6; 5DBN-*p*-Me, 118018-56-7; 7DBN-*p*-Me, 50445-70-0; 3T nylon (SRU), 35483-54-6; 3T nylon (copolymer), 103691-99-2; 5T nylon (SRU), 32985-25-4; 5T nylon (copolymer), 32761-06-1.

Supplementary Material Available: Tables VIa–c and VIIa–c listing H-atom coordinates, U_{iso}, anisotropic thermal parameters, and their esd's for 3DBN-*p*-OMe, 5DBN-*p*-Me, and 7DBN-*p*-Me (6 pages); tables of calculated and observed structure factors (41 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Brisson, J.; Brisse, F. *Macromolecules* **1986**, *19*, 2632.
(2) Brisson, J.; Gagné, J.; Brisse, F., submitted for publication in *Can. J. Chem.*
(3) Brisson, J.; Brisse, F. *Can. J. Chem.* **1985**, *12*, 3390.
(4) Palmer, A.; Brisse, F. *Acta Crystallogr.* **1980**, *B36*, 1447.
(5) Shashoua, V. E.; Eareckson, W. M. *J. Polym. Sci.* **1959**, *40*, 343.
(6) The programs used for the structure calculations are modified versions of NRC-2, data reduction; NRC-10, bond distances and angles; NRC-22, mean planes; FORDAP, Fourier and Patterson maps (Zalkin, A.); and NUCLS, least-squares refinement.
(7) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, L.; Declercq, J.-P.; Woolfson, M. M. MULTAN80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Universities of York, England, and Louvain, Belgium, 1980.
(8) Sheldrick, G. M. SHELX, Program for Crystal Structure Solution. University of Göttingen Federal Republic of Germany, 1984.
(9) Ahmed, F. R.; Hall, S. R.; Pippy, M. E.; Huber, C. P. *J. Appl. Crystallogr.* **1973**, *6*, 309 (Accession Nos. 133-147).
(10) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.
(11) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1965**, *A24*, 321.
(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(13) Johnson, C. K. ORTEP. Report ORNL-3794, 1965; Oak Ridge National Laboratories, Oak Ridge, TN.
(14) Harkema, S.; Gaymans, R. J.; Van Hummel, G. J. *Acta Crystallogr.* **1980**, *B36*, 3182.
(15) Pineault, C.; Brisse, F. *Acta Crystallogr.* **1983**, *C39*, 1437.
(16) Brisson, J.; Brisse, F. *Acta Crystallogr.* **1982**, *B38*, 2663.
(17) Pineault, C.; Brisse, F. *Acta Crystallogr.* **1983**, *C39*, 1434.
(18) Sarko, A. CRSP, Crystallographic Packing Program. Modified by S. Pérez and V. Tran, CERMAV, Grenoble, 1979.
(19) Statton, W. O. *Ann. N. Y. Acad. Sci.* **1959**, *83*, 27.
(20) Grenier-Loustalot, M.-F.; Bocelli, G. *Eur. Polym. J.* **1984**, *20*, 9757.