

Crystal structure of poly(butylene-2,6-naphthalate)

Hirotooshi Koyano¹, Yuzo Yamamoto², Yasushi Saito², Takeshi Yamanobe¹
and Tadashi Komoto¹ *

*Departments of Chemistry¹ and Biological and Chemical Engineering²,
Gunma University, Tenjin-cho, Kiryu, Gunma 376, Japan*

ABSTRACT

The two crystal structures of poly(butylene-2,6-naphthalate) (PBN) have been determined by X-ray diffraction. The space group is $P\bar{1}$ for both forms. The unit cell parameters of B form are $a = 4.55\text{\AA}$, $b = 6.43\text{\AA}$, c (fiber axis) = 15.31\AA , $\alpha = 110.1^\circ$, $\beta = 121.1^\circ$ and $\gamma = 100.6^\circ$. The major difference of crystal structure between A and B forms lies in the conformation of four methylene group sequences: $\overline{\text{SGTGS}}$ for A form and $\overline{\text{TST}\bar{\text{T}}}$ for B form.

(keywords: polymer, poly(butylene-2,6-naphthalate), X-ray diffraction, crystal structure, conformation)

*To whom correspondence should be addressed.

INTRODUCTION

The crystal structures of poly(ethylene terephthalate) (PET)^{1,2)}, poly(ethylene-2,6-naphthalate) (PEN)³⁾ and poly(butylene terephthalate) (PBT)^{4,5)} have been reported. The structural study on poly(butylene-2,6-naphthalate) (PBN) (Fig. 1) was only reported by Watanabe⁶⁾.

Two crystal modifications A and B of PBN have been reported⁶⁾. The form A assigned to the structure formed by uniaxial drawing of the undrawn PBN specimen has the triclinic form having a unit cell with $a = 0.487\text{nm}$, $b = 0.622\text{nm}$, $c = 1.436\text{nm}$ (fiber axis), $\alpha = 100.78^\circ$, $\beta = 126.90^\circ$ and $\gamma = 97.93^\circ$. One repeating unit is contained in the unit cell. However, neither the unit cell parameters of the form B nor the conformations and crystal structures of the two forms were determined.

In this paper, we will report on the crystal structures of the A and B form and the double orientation and tilting of the chains as studied by X-ray diffraction.

EXPERIMENTAL

Specimens

Unoriented crystalline PBN film with thickness of $100\mu\text{m}$ was used as the original specimen. Two kinds of uniaxially drawn films were prepared. One is the film drawn to ca. 3 times at room temperature and annealed under tension at 200°C in a silicone bath. The other is the film drawn to ca. 9 times at 180°C . The former contains A and B forms, while the latter only B form as will be mentioned.

A doubly oriented specimen was prepared by drawing the original film at 170°C to ca. 3 times keeping the film width constant.

X-ray photographs

X-ray photographs were taken by using Nickel-filtered CuK α radiation (from a Rigaku Denki, Rotaflex X-ray generator or Geigerflex X-ray generator). The X-ray fiber

patterns are shown in Fig. 2: (a) the sample containing A and B forms, (b) the sample containing only B form. From Fig. 2, 23 independent reflections were observed for both A and B form. For estimating intensity, the multiple-film method was applied to the X-ray fiber patterns, and the diffraction spots were measured by visual comparison with a standard intensity scale. The usual corrections were made for spot intensities.

X-ray photograph of doubly oriented film taken by plate camera is shown in Fig. 3, where the incident X-ray beam was parallel to the drawing direction. On this X-ray photograph, the reflections of two modifications were recorded.

Density

Density measurement was carried out at 25°C in a solution of heptane and carbon tetrachloride in a density-gradient column.

ANALYSIS AND RESULT

Unit cells and space groups

Diffraction spots on fiber diagram shown in Figs. 2(a) and (b) were found to be displaced from the position where they should appear as a straight line in the case of uniaxial oriented sample. This displacement is caused by the so-called "tilting" which was reported for PET by Daubeny et al.¹⁾ and PBT by Yokouchi et al.⁴⁾. The observed reflections were indexed and the unit cells were determined by the method applied to PET¹⁾ and PBT⁴⁾. The tilting occurred in $1\bar{1}0$ plane by ca. 5° for A form of PBN and in $3\bar{2}0$ plane by ca. 5° for B form. The reciprocal lattice diagrams showing the displacements are shown in Fig. 4. The calculated positions (dots in Fig. 4) were estimated by the following equation.

$$\zeta = z \cos \phi - x \sin \phi$$

where z is the normal untilted height of the reciprocal lattice layer, ϕ the angle of tilt and x the measured distance of the lattice point from the tilt line in the reciprocal lattice diagram.

As shown in Fig. 5, the calculated positions coincide well with the observed positions.

The equatorial reciprocal lattice nets obtained from Fig. 3 are also shown in Fig. 5. The dimension of a^* , b^* and γ^* were estimated from the reciprocal lattice nets .

Unit cell parameters of A and B forms obtained above are listed in Table 1. The diffraction spots shown in Fig. 2(b) can be indexed by the unit cell of B form. On the other hand, the diffraction spots in Fig. 2(a) can be indexed by the unit cells of A and B forms.

The density of A and B forms, calculated by assuming one monomer unit in the unit cell, is reasonable as compared with the observed density .

The space group for two crystal forms is either P1 or $P\bar{1}$. If the molecules possess symmetry centers, the space group is the latter. In this work, it is assumed that PBN monomer units have the symmetry center at the midpoint of four methylene group sequences ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$). Therefore, the space groups of both crystal forms are assumed to be $P\bar{1}$.

Molecular models

The numbering of atoms and internal rotation angles are shown in Fig. 6. The bond lengths and bond angles used in this work are standard values and listed in Table 2. The 2,6-naphthalene dicarboxylic acid residue was assumed to be planar because the conjugated system of this part should be planar. The conformations of the four methylene group sequences for A and B forms were estimated from the conformation of this part for α and β forms of PBT reported by Yokouchi et al⁴⁾ [α form: $\overline{\text{GGTGG}}(-88^\circ, -68^\circ, 180^\circ, 68^\circ, 88^\circ)$ and β form: $\overline{\text{TSTST}}(-179^\circ, 113^\circ, 180^\circ, -113^\circ, 179^\circ)$], respectively, because the analogy of crystal structure of PBN to that of PBT is expected. Thus, the conformations of four methylene group sequences were determined to be approximately $\overline{\text{SGTGS}}(-125^\circ, -60^\circ, 180^\circ, 60^\circ, 125^\circ)$ for A form and $\overline{\text{TSTST}}(180^\circ, 110^\circ, 180^\circ, -110^\circ, 180^\circ)$ for B form.

The fiber period calculated from these molecular models is identical with the length of c axis.

Crystal structures

The primary crystal structure models for A and B forms were determined by rotating the molecular models around c axis. The atomic coordinates calculated from these crystal structure models were used to estimate the structure factors. On the calculation of the structure factors, the isotropic temperature factors B were assumed to be 5.7\AA^2 and 5.5\AA^2 for A and B forms, respectively. At this stage, the discrepancy factor $R = \sum ||F_{obs}| - |F_{cal}|| / \sum |F_{obs}|$ for all the observed reflections were 21.8% for A form and 27.0% for B form.

These primary crystal structures were then refined with constrained least-squares method⁷⁾ (the software performing the constrained least squares was made in FORTRAN77 language by ourselves). The internal rotation angles (τ_1, τ_2 and τ_3 shown in Fig. 6) and the isotropic temperature factors B were chosen as the main parameters which should be detraind in refining. Other internal rotation angles, the bond lengths and the bond angles were fixed. On refining, unobserved reflections were taken into account with the weight factor of 0.5 and the intensity as half the weakest observed intensity. After refining, the internal rotation angles (τ_1, τ_2 and τ_3) are 59° , 123° and -177° for A form and -107° , 188° and -178° for B form, respectively and the isotropic temperature factors are 5.9\AA^2 for A form and 14.7\AA^2 for B form. At this stage, the R factors for all the observed reflections decreased to 17.4% for A form and 21.8% for B form.

The R factors are much improved by introducing the anisotropic temperature factor as,

$$\exp\left[-\left(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2lhB_{31}\right)\right]$$

with the coefficients obtained by least-squares method. Each coefficient is given in Table 3. The resultant R factors for all the observed reflections are 15.4% for A form and 19.4% for B form.

Table 4 lists the final atomic coordinates. The calculated and observed values of the structure factor for final crystal structures are listed in Table 5. The final crystal structures for A and B forms are shown in Figs. 7 and 8, respectively.

Table 6 lists the interatomic distances between the adjacent molecules. When these distances are compared with the sums of van der Waals radii⁸⁾ for each atom pair, the interatomic distances between the adjacent molecules were found to be reasonable..

DISCUSSION

Molecular and crystal structures

As listed in Table 1, the cell dimensions of A and B forms are very similar to each other except for the fiber identity period. The molecular packings of the two crystal forms are almost similar shown in Figs. 7 and 8, respectively. The main difference between two modifications can be seen in fiber period, due to the molecular conformations of four methylene group sequences as in the case of PBT⁴⁾. In PBN, the conformation of the four methylene group sequence is $\overline{S}GTGS$ for A form and $T\overline{S}T\overline{S}T$ for B form. Consequently, the main chain of B form is more extended than A form.

The crystal structures of A and B forms of PBN are similar to those of α and β form of PBT⁴⁾, respectively. Thus, the crystal structures of A and B forms of PBN are considered to be equivalent to the structures obtained by replacing benzene ring in the crystal structure of α and β forms of PBT⁴⁾ by naphthalene ring, respectively.

Double orientation

From the X-ray photograph shown in Fig. 3, the equatorial reciprocal lattices for the doubly oriented sample of the A and B form were obtained as shown in Fig. 5. From the reciprocal lattice point 010 for A and B forms, it was found that the film surface coincides

approximately with (010) of the two modifications. The (010) of these modifications is essentially parallel to the plane containing naphthalene ring. Consequently, it can be said that the naphthalene rings are arranged nearly parallel to the film surface in the specimen obtained by drawing at constant width. The double orientation of PBN is very similar to those in rolled samples of PET⁹⁾ and PBT⁴⁾.

Irregularity in the crystal structure

The coefficients of anisotropic temperature factors for both A and B forms qualitatively indicate that the regularity in the direction to the main chain is less than in the lateral direction to the main chain. The reason for the less regularity in the direction along the main chain may be that the lateral regularity is kept strong by the stacking of naphthalene rings, while that in the direction along the main chain is not so strong as the lateral regularity because PBN does not have the interchain interaction acting between specific positions (e.g. the hydrogen bond).

REFERENCES

- 1) Daubeny, R. P., Bunn, C. W. and Brown, C. J., *Proc. Roy. Soc.*, **226A**, 531 (1954)
- 2) Fu, Y., Busing, W. R., Jin, Y., Afholter, K. A. and Wunderlich, B., *Macromolecules*, **26**, 2187 (1993)
- 3) Z. Mencik, Z., *Chem. Prum.*, **17**, 78 (1976)
- 4) Yokouchi, M., Sakakibara, Y., Chatani, Y., Tadokoro, H., Tanaka, T., and Yoda, K., *Macromolecules*, **9**, 266 (1976)
- 5) Hall, I. H. and Pass, M. G., *Polymer*, **17**, 807 (1976)
- 6) Watanabe, H., *Kobunshi Ronbunshu*, **33**, 299 (1976)
- 7) Arnott, S. and Eonacott, A. J., *Polymer*, **7**, 157 (1966)
- 8) Bunn, C. W., *Trans. Faraday Soc.*, **35**, 482 (1939)
- (9) Tadokoro, H., Tatsuka, K. and Murahashi, S., *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 233 (1973)

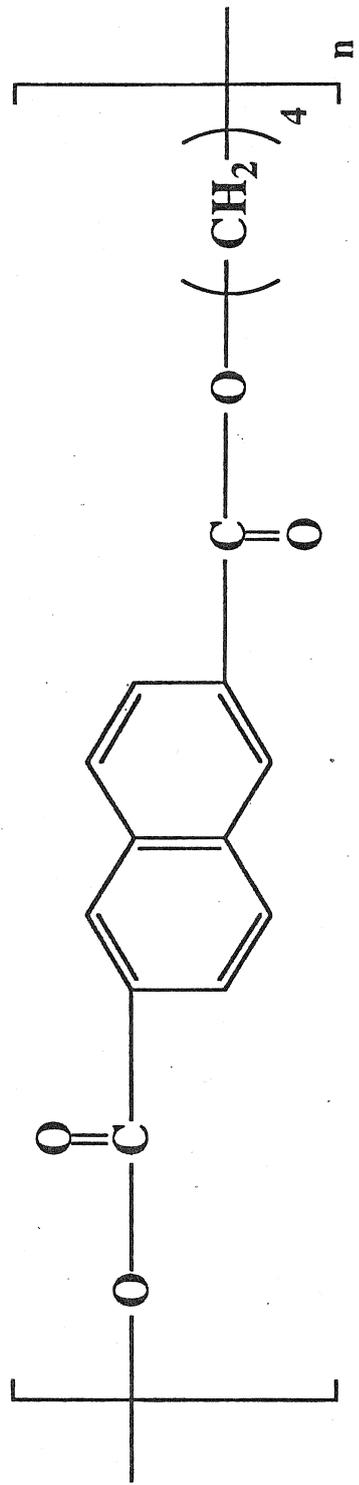
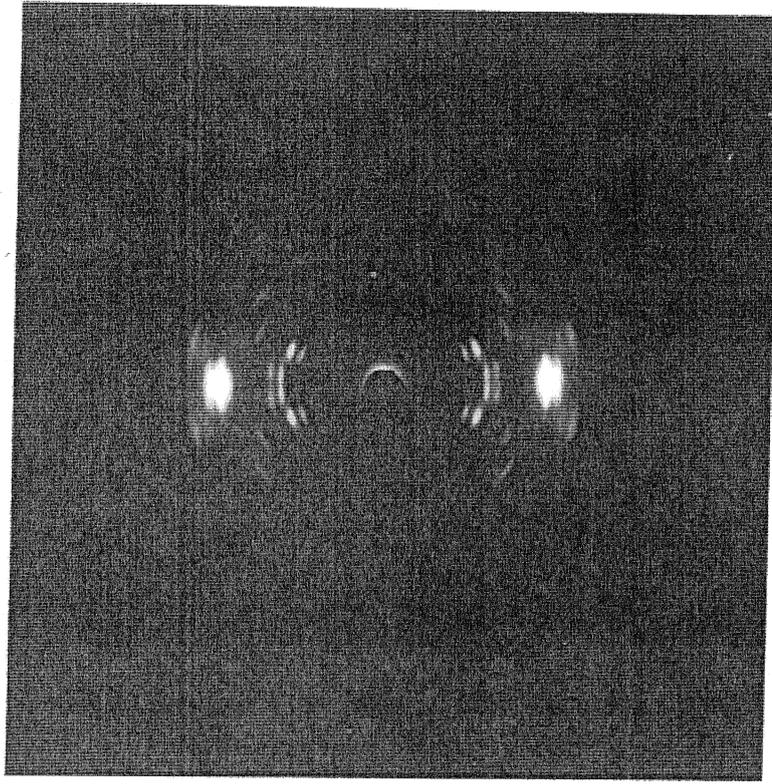
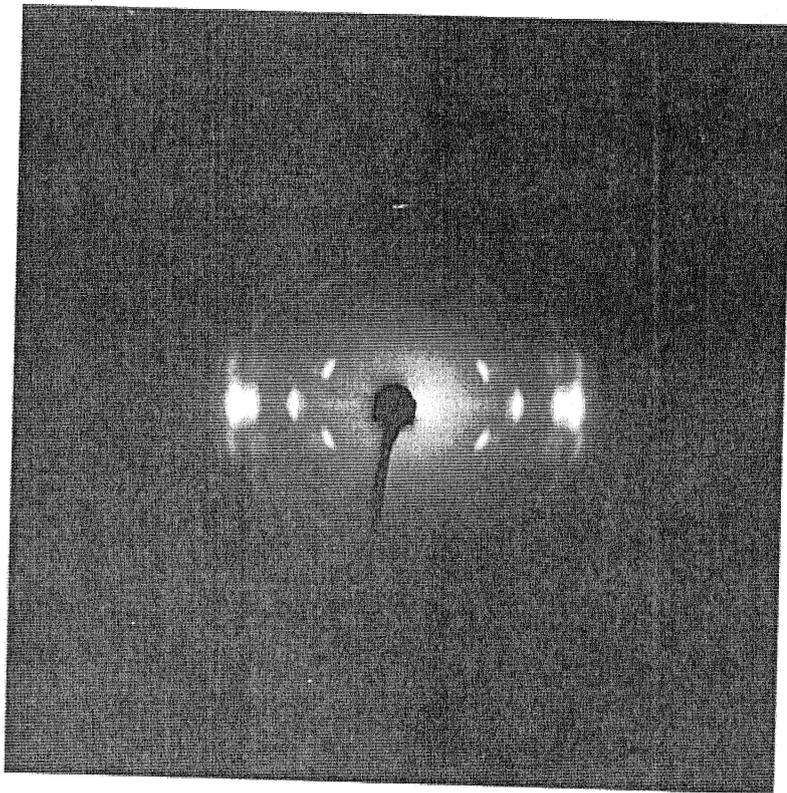


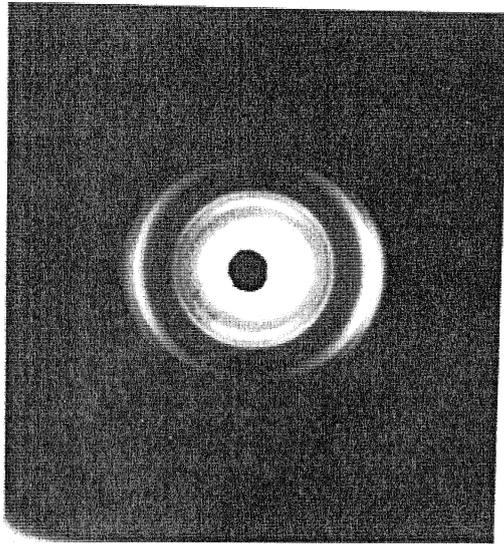
Figure 1. Koyano et al

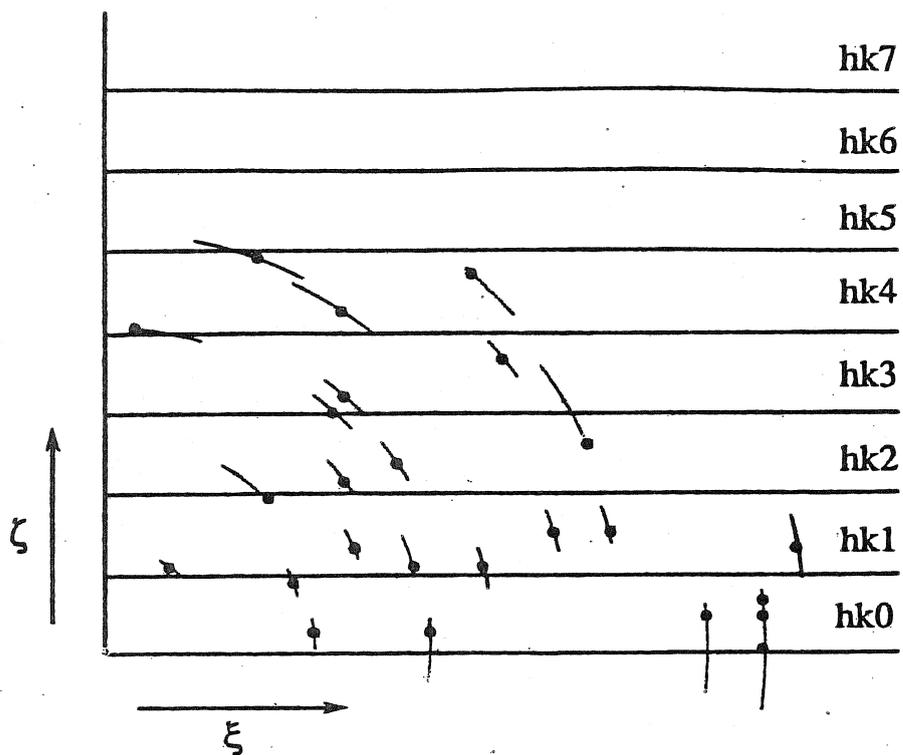


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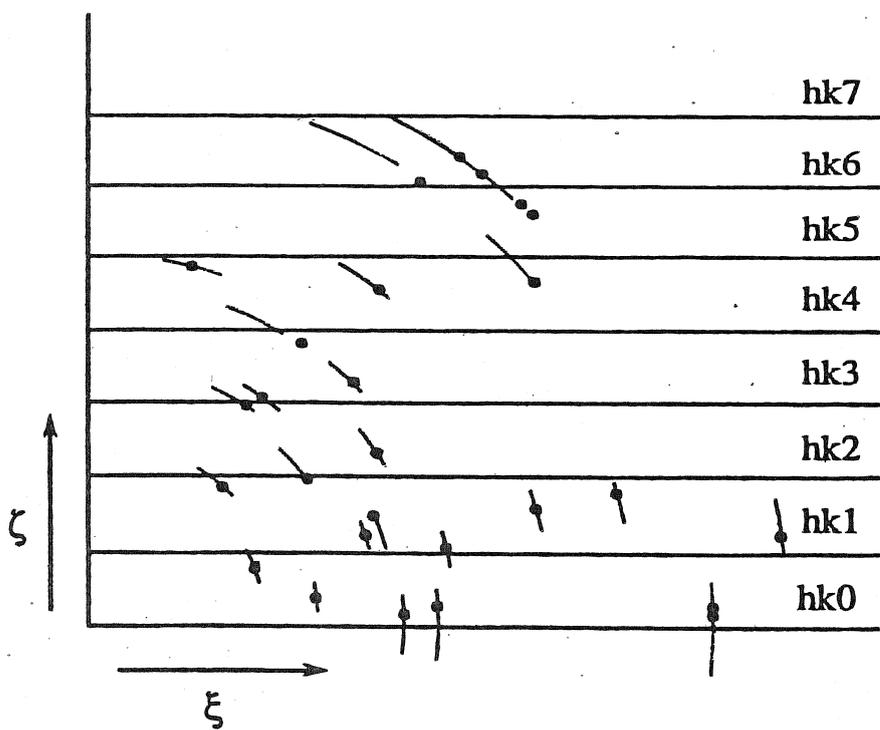


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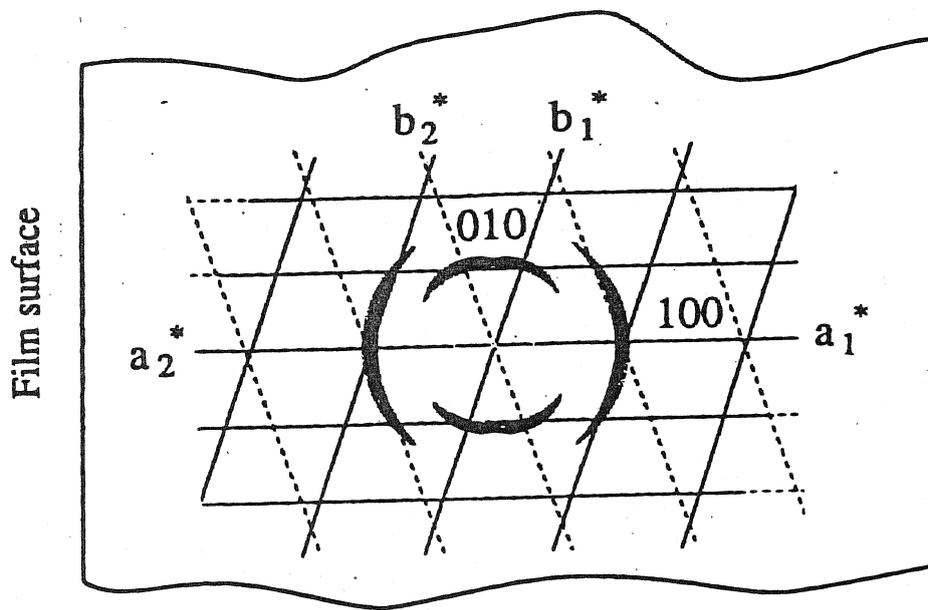




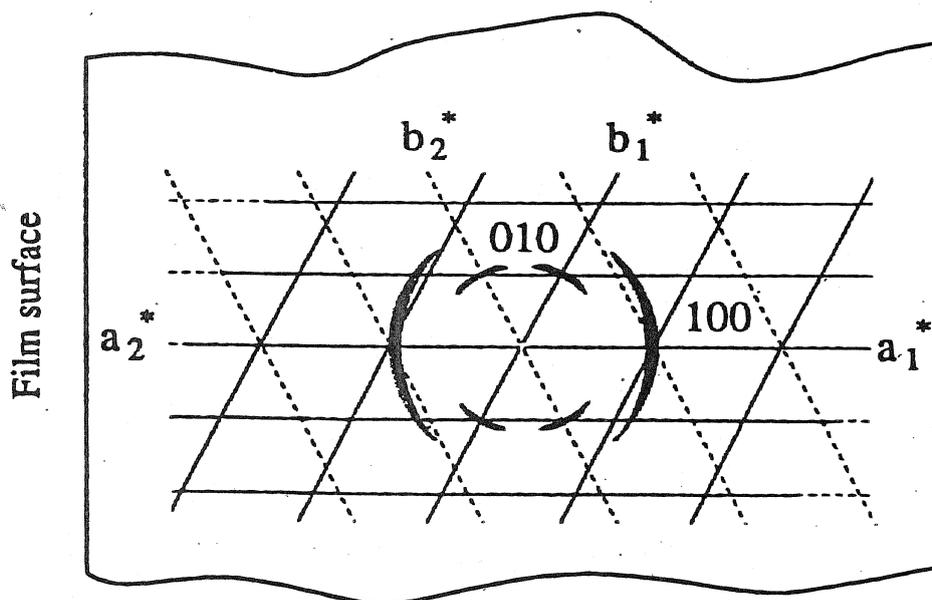
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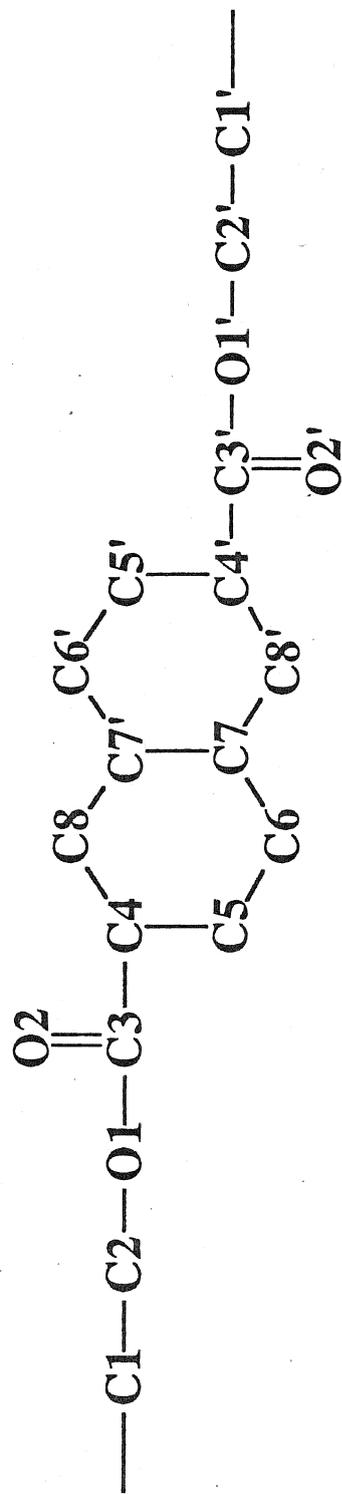
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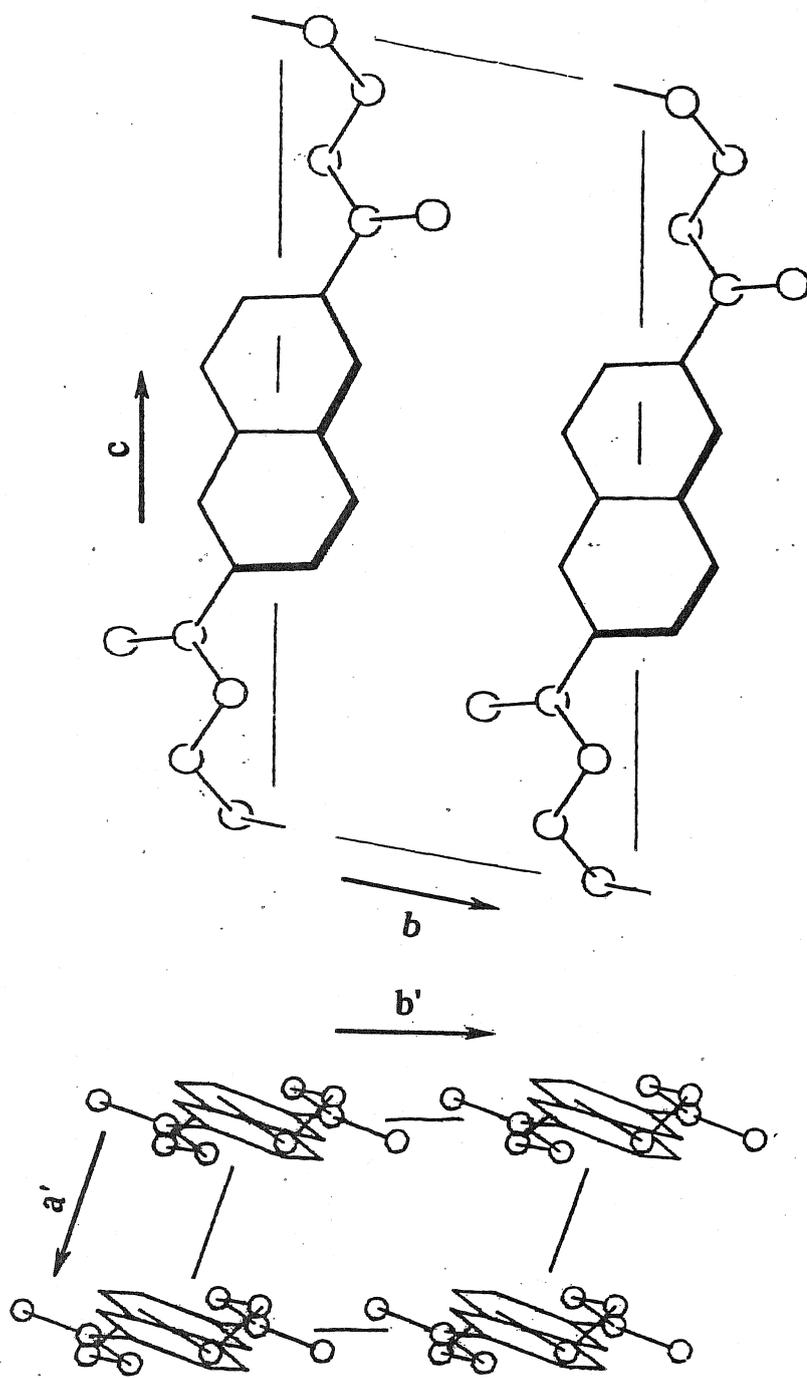


(a)



(b)





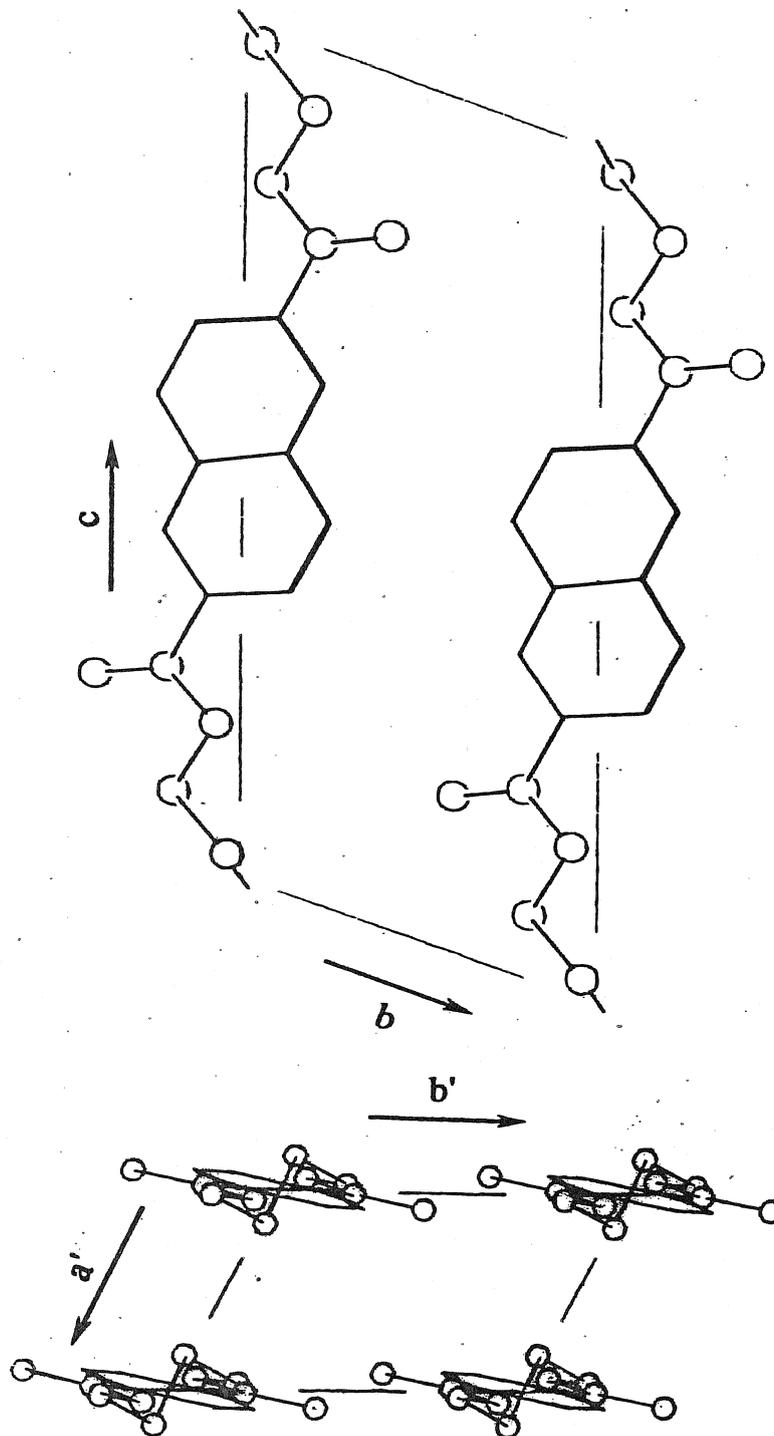


Table 1. Crystallographic data for Poly(butylene-2,6-naphthalate).

	A form ⁶⁾	B form ^{a)}
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}^a)$	$P\bar{1}$
Cell parameters		
a / Å	4.87	4.55
b / Å	6.22	6.43
c / Å ^{b)}	14.36	15.31
$\alpha / ^\circ$	100.78	110.1
$\beta / ^\circ$	126.90	121.1
$\gamma / ^\circ$	97.93	100.6
Numbers of repeating unit per unit cell	1	1
Density / g cm ⁻³		
Observed	1.33 ^{c)}	1.34 ^{d)}
Calculated	1.36 ^{a)}	1.39
Observed reflection	23 ^{a)}	23

a) This work.

b) Fiber axis.

c) The sample containing A and B forms.

d) The sample containing only B form.

Table 2. Bond lengths and bond angles.

Bond lengths (Å)		Bond angles (deg)	
C1-C1'	1.54 ⁽¹¹⁾	C2-C1-C1'	109 ⁽¹¹⁾
C2-C1	1.54 ⁽¹¹⁾	O3-C2-C1	110 ⁽¹¹⁾
O3-C2	1.43 ⁽¹¹⁾	C4-O3-C2	111 ⁽¹¹⁾
C4-O3	1.36 ⁽¹¹⁾	C5-C4-O3	114 ⁽¹¹⁾
C5-C4	1.49 ⁽¹¹⁾	C6-C5-C4	120
C6-C5	1.41 ⁽⁸⁾	C7-C6-C5	120
C7-C6	1.40 ⁽⁸⁾	C8-C7-C6	120
C8-C7	1.41 ⁽⁸⁾	C8'-C8-C7	120
C8'-C8	1.40 ⁽⁸⁾	C9-C5-C4	120
C9-C5	1.39 ⁽⁸⁾	C10-C4-O3	123 ⁽⁸⁾
O10-C4	1.23 ⁽¹¹⁾		

Table 3. Anisotropic temperature factor coefficients.

	A form	B form
B_{11}	0.1575 (8.6Å ²) ^{a)}	0.2685 (13.0Å ²)
B_{22}	0.0547 (7.3Å ²)	0.1069 (12.4Å ²)
B_{33}	0.0231 (10.8Å ²)	0.0427 (21.4Å ²)
B_{12}	0.0260 (7.0Å ²)	0.0903 (18.3Å ²)
B_{23}	0.0018 (1.3Å ²)	0.0214 (9.9Å ²)
B_{31}	0.0297 (7.4Å ²)	0.0700 (17.3Å ²)

a) The value in parenthesis is the coefficients of general temperature factor.

Table 4. Fractional atomic coordinates.

(a) A form

Atom	x	y	z
C1	-0.106	-0.127	-0.020
C2	0.113	-0.218	0.088
O1	0.154	-0.090	0.191
C4	0.020	-0.232	0.226
C5	0.033	-0.110	0.329
C6	0.175	0.133	0.381
C7	0.187	0.249	0.477
C8	0.057	0.122	0.522
C9	-0.095	-0.234	0.373
O2	-0.101	-0.444	0.177

(b) B form

Atom	x	y	z
C1	0.175	0.011	0.055
C2	0.031	-0.178	0.081
O1	0.059	-0.054	0.185
C3	-0.016	-0.212	0.219
C4	-0.002	-0.097	0.324
C5	0.083	0.156	0.379
C6	0.096	0.265	0.479
C7	0.024	0.122	0.523
C8	-0.074	-0.238	0.369
O2	-0.089	-0.431	0.167

Table 5. Observed and calculated structure factors.

(a) A form

hkl	F _{obs}	F _{cal}	hkl	F _{obs}	F _{cal}	hkl	F _{obs}	F _{cal}
010	32.9	31.4	$\bar{2}\bar{1}5$	8.0	15.0	$\bar{1}02$	-	1.4
100	65.9	63.1	Unobserved reflection			$\bar{1}\bar{1}2$	-	2.0
$\bar{1}\bar{1}0$		29.4	$2\bar{1}0$	-	6.0	013	-	4.0
$\bar{1}\bar{3}0$	14.6	14.5	120	-	3.5	$\bar{1}\bar{1}3$	-	10.2
200	18.2	5.9	110	-	3.6	$0\bar{2}3$	-	19.9
$\bar{2}\bar{2}0$		2.8	$\bar{1}\bar{2}0$	-	9.5	$\bar{1}\bar{2}3$	-	18.6
030		17.1	020	-	12.4	$\bar{1}03$	-	0.4
001	14.1	9.0	201	-	2.2	$\bar{1}\bar{1}3$	-	7.5
$0\bar{1}\bar{1}$	44.7	41.4	$2\bar{2}\bar{1}$	-	5.7	$\bar{2}\bar{1}3$	-	8.0
011	32.1	21.4	121	-	10.2	$\bar{2}03$	-	5.5
$\bar{1}\bar{1}\bar{1}$	21.4	18.6	101	-	10.2	$\bar{2}\bar{1}3$	-	1.4
$\bar{1}\bar{1}\bar{1}$	53.4	54.9	$\bar{1}\bar{2}\bar{1}$	-	7.0	014	-	0.2
021	16.9	14.8	$\bar{1}\bar{3}\bar{1}$	-	4.0	004	-	0.7
111	10.9	9.3	031	-	4.1	$0\bar{1}4$	-	6.2
$2\bar{1}\bar{1}$	23.9	21.6	$0\bar{2}\bar{1}$	-	1.7	$0\bar{2}4$	-	0.5
$\bar{2}\bar{3}\bar{1}$		3.3	031	-	4.1	$\bar{1}\bar{1}4$	-	2.1
$0\bar{1}\bar{2}$	6.5	2.7	$\bar{1}\bar{3}\bar{1}$	-	6.4	$\bar{2}\bar{1}4$	-	4.5
$\bar{1}\bar{1}\bar{2}$	32.2	32.4	$\bar{1}\bar{2}\bar{1}$	-	0.7	$\bar{2}04$	-	7.8
012	21.1	16.0	$\bar{1}0\bar{1}$	-	9.2	005	-	9.4
$0\bar{1}\bar{3}$	13.7	15.1	$\bar{1}\bar{1}\bar{1}$	-	4.2	$0\bar{1}5$	-	4.2
003	13.7	13.4	$\bar{1}\bar{2}\bar{1}$	-	2.4	$0\bar{2}5$	-	3.8
$\bar{1}\bar{2}\bar{3}$	10.3	15.7	$\bar{1}\bar{3}\bar{1}$	-	6.2	$\bar{1}\bar{1}5$	-	6.8
$\bar{1}04$	1.2	2.5	$\bar{2}\bar{2}\bar{1}$	-	7.1	$\bar{1}05$	-	14.0
$\bar{2}\bar{1}4$	8.3	2.2	$\bar{2}\bar{1}\bar{1}$	-	8.4	$\bar{1}\bar{2}5$	-	0.7
$\bar{1}\bar{2}4$		0.5	$\bar{2}0\bar{1}$	-	4.8	$\bar{2}\bar{1}5$	-	5.8
$\bar{1}\bar{1}4$	5.9	2.1	$\bar{2}\bar{1}\bar{1}$	-	7.2	$\bar{2}05$	-	5.0
$\bar{1}\bar{1}5$	4.6	7.5	002	-	0.09			

(b) B form

hkl	F _{obs}	F _{cal}	hkl	F _{obs}	F _{cal}	hkl	F _{obs}	F _{cal}
010	36.9	40.0	Unobserved reflection			$\bar{1}\bar{1}2$	-	0.7
$\bar{1}\bar{1}0$	38.7	42.2	200	-	13.3	013	-	3.1
100	71.2	73.1	120	-	0.3	$0\bar{2}3$	-	3.5
$2\bar{1}0$	18.1	14.5	110	-	7.3	$\bar{1}23$	-	1.5
$2\bar{2}0$		6.4	$\bar{1}20$	-	6.7	$\bar{1}13$	-	7.4
$0\bar{1}1$	41.6	34.1	$\bar{1}30$	-	9.2	$\bar{1}\bar{1}3$	-	12.2
$\bar{1}11$	27.6	23.5	030	-	4.8	$\bar{1}23$	-	7.0
011	28.4	24.5	020	-	1.4	$\bar{2}13$	-	0.6
$\bar{1}\bar{1}1$	41.9	43.5	$2\bar{2}1$	-	8.6	$\bar{2}03$	-	2.8
$\bar{1}21$	24.4	17.5	111	-	6.3	004	-	4.5
021	22.0	17.9	101	-	5.2	$0\bar{1}4$	-	2.3
$2\bar{1}1$	23.5	17.4	$\bar{1}21$	-	3.1	$0\bar{2}4$	-	3.9
$0\bar{1}2$	10.3	7.1	$\bar{1}31$	-	1.2	$\bar{1}14$	-	1.4
$\bar{1}02$	11.0	1.8	031	-	6.0	$\bar{1}04$	-	0.2
$\bar{1}12$	26.2	28.9	001	-	7.7	$\bar{1}24$	-	0.5
$0\bar{1}3$	8.4	10.8	$0\bar{2}1$	-	10.9	$\bar{2}14$	-	6.5
$\bar{1}03$	18.6	8.9	$0\bar{3}1$	-	1.5	$\bar{2}04$	-	1.3
003	14.4	15.9	$\bar{1}31$	-	13.1	005	-	3.0
$\bar{1}\bar{1}4$	14.1	2.6	$\bar{1}01$	-	6.1	$0\bar{1}5$	-	1.2
$\bar{1}\bar{1}5$	1.3	1.4	$\bar{1}\bar{1}1$	-	4.1	$0\bar{2}5$	-	2.3
$\bar{1}25$	12.4	0.4	$\bar{1}21$	-	5.6	$0\bar{3}5$	-	2.6
$\bar{2}15$	6.8	5.2	$\bar{2}31$	-	8.3	$\bar{1}15$	-	2.4
$\bar{2}06$	12.7	9.0	$\bar{2}21$	-	2.1	$\bar{1}05$	-	12.5
$0\bar{1}6$	20.6	2.8	$\bar{2}11$	-	6.6	$\bar{2}15$	-	2.2
$\bar{2}16$		13.9	$\bar{2}01$	-	3.2	$\bar{2}05$	-	9.5
$\bar{1}26$		11.9	$\bar{2}\bar{1}1$	-	1.4	$0\bar{2}6$	-	5.0
$\bar{1}06$		11.5	002	-	0.06	$\bar{1}16$	-	1.1
			$0\bar{2}2$	-	7.6	$\bar{2}16$	-	1.7

Table 6. Interatomic distances.

(a) A form

Atom pair	Distance /Å	Atom pair	Distance /Å	Atom pair	Distance /Å
C2(0)-C3(1) ^a	3.62	C4(0)-C8(1)	4.11	C6(0)-O2'(1)	3.96
C2(0)-C4(1)	3.49	C4(0)-C4'(1)	3.96	C7(0)-O1'(1)	3.64
C2(0)-C5(1)	4.07	C4(0)-C5'(1)	3.66	C7(0)-C3'(1)	3.52
C2(0)-C8(1)	3.60	C4(0)-C6'(1)	3.47	C7(0)-C4'(1)	3.61
C2(0)-C9(1)	3.81	C4(0)-C7'(1)	3.61	C7(0)-C5'(1)	3.83
O1(0)-C3(1)	4.18	C4(0)-C8'(1)	4.07	C7(0)-O2'(1)	4.01
O1(0)-C4(1)	3.51	C5(0)-C6(1)	4.14	C8(0)-C4'(1)	4.07
O1(0)-C5(1)	3.81	C5(0)-C7(1)	3.50	C8(0)-C5'(1)	3.51
O1(0)-C6(1)	3.96	C5(0)-C4'(1)	3.66	C8(0)-C6'(1)	3.60
O1(0)-C7(1)	3.83	C5(1)-C5'(1)	3.88	O2(0)-C8(1)	3.73
O1(0)-C8(1)	3.36	C5(0)-C6'(1)	3.96	O2(0)-C6'(1)	3.96
O1(0)-C7'(1)	3.64	C5(0)-C7'(1)	3.83	O2(0)-C7'(1)	4.01
C3(0)-C4(1)	4.11	C5(0)-C8'(1)	3.51	C5(0)-C6'(2)	3.84
C3(0)-C7(1)	4.01	C6(0)-C7(1)	4.10	C6(0)-C5'(2)	3.84
C3(0)-C8(1)	3.48	C6(0)-C3'(1)	3.69	C6(0)-C6'(2)	3.70
C3(0)-C6'(1)	3.67	C6(0)-C4'(1)	3.47	C5(0)-O2(3)	4.05
C3(0)-C7'(1)	3.53	C6(0)-C5'(1)	3.96	C6(0)-C8'(3)	3.87
C4(0)-C7(1)	3.81	C6(0)-C8'(1)	3.60	C6(0)-C6'(3)	3.97

(b) B form

Atom pair	Distance /Å	Atom pair	Distance /Å	Atom pair	Distance /Å
C1(0)-C1'(1)	4.10	C3(0)-C7(1)	3.92	C8(0)-C8'(1)	4.09
C1(0)-C2(1)	4.16	C4(0)-C6(1)	3.96	O2(0)-C4(1)	3.89
C1(0)-O1(1)	3.63	C4(0)-C7(1)	3.61	O2(0)-C8(1)	3.60
C1(0)-C3(1)	4.10	C4(0)-C7'(1)	3.88	O2(0)-C7'(1)	4.02
C1(0)-C5(1)	4.09	C4(0)-C8'(1)	4.01	C1(0)-O2(2)	3.53
C2(0)-O1(1)	3.89	C5(0)-C6(1)	3.86	C5(0)-C5'(2)	3.96
C2(0)-C3(1)	3.80	C5(0)-C7(1)	3.76	C5(0)-C6'(2)	3.67
C2(0)-C4(1)	3.78	C5(0)-C8'(1)	3.90	C6(0)-C5'(2)	3.67
C2(0)-C5(1)	3.91	C6(0)-C8'(1)	3.89	C6(0)-C6'(2)	3.89
O1(0)-C4(1)	3.78	C7(0)-C3'(1)	3.92	C1(0)-O2(3)	4.09
O1(0)-C5(1)	3.60	C7(0)-C4'(1)	3.89	C5(0)-C8(3)	4.13
O1(0)-C6(1)	3.86	C7(0)-C8'(1)	3.97	C5(0)-C6'(3)	4.08
O1(0)-C8(1)	4.17	C7(0)-O2'(1)	4.02	C6(0)-C8(3)	4.11
C3(0)-C4(1)	3.83	C8(0)-C7(1)	3.96	C6(0)-C5'(3)	4.08
C3(0)-C5(1)	3.95	C8(0)-C4'(1)	4.01	C6(0)-C6'(3)	3.24
C3(0)-C6(1)	3.99	C8(0)-C5'(1)	3.90	C6(0)-C7'(3)	4.09
C3(0)-C7(1)	3.91	C8(0)-C6'(1)	3.89	C7(0)-C6'(3)	4.09
C3(0)-C8(1)	3.74	C8(0)-C7'(1)	3.98		

a) Distance between atoms of molecules at (x,y,z,) and (1)(x+1, y,z), (2)(x+1,y+1,z), (3)(x,y+1,z).

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Table 6 (continued)