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Crystal structure identification of poly(trimethylene 2,6-naphthalate) β-form crystal by X-ray diffraction and molecular modeling

Young Gyu Jeong[a], Won Ho Jo[a,*], Sang Cheol Lee[b,*]

[a]Hyperstructured Organic Materials Research Center and School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea
[b]School of Advanced Materials and Systems Engineering, Kumoh National University of Technology, Kumi 730-701, South Korea

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Abstract

X-ray powder diffraction and molecular modeling are used to identify the crystal structure and chain conformation of poly(trimethylene 2,6-naphthalate) (PTN) β-form crystal. The unit cell of PTN β-form crystal was determined to be a triclinic with dimensions of $a = 0.4665$ nm, $b = 0.7014$ nm, $c = 2.2177$ nm, $\alpha = 100.85°$, $\beta = 88.78°$ and $\gamma = 120.63°$, and the space group of the crystal is identified as $P\bar{1}$. The observed crystal density of 1.37 g cm^{-3} and the determined dimensions of unit cell indicate that the unit cell contains one polymer chain with two repeating units. In the unit cell, each trimethylene unit in PTN backbone is in *gauche/gauche* conformation and neighboring naphthalene units are in face-to-face type arrangement, forming π-stacks that lead to the lowest energy of the unit cell.

Keywords: Crystal structure; β-Form crystal; Poly(trimethylene 2,6-naphthalate)

1. Introduction

Poly(*m*-methylene 2,6-naphthalate)s (*m* denotes the number of methylene group) with the chemical structure as shown in Fig. 1 have attracted considerable interests from industry and academia [1], since 2,6-naphthalenedicarboxylic acid becomes available in commercial quantity.

It has been reported that poly(ethylene 2,6-naphthalate) (PEN, $m = 2$), the most well known polymer among this family, has two crystal structures, α-form and β-form, depending upon the crystallization temperature [2–5]. The α-form is a triclinic unit cell with a fully extended chain and the β-form is a monoclinic cell containing four chains with non-*trans* conformation. It has also been reported that poly(butylene 2,6-naphthalate) (PBN, $m = 4$) has two crystal structures, i.e. A-form and B-form, depending upon the crystallization temperature and the elongational stress [6–8]. The major difference between two crystal structures of PBN is seen in the fiber period, due to the difference in the molecular conformation of butylene unit as in the case of poly(butylene terephthalate) [9,10], i.e. the backbone chain in the B-form crystal is more extended than that of the A-form crystal. Recently, we have investigated the crystal structures and thermal properties of poly(pentamethylene 2,6-naphthalate) (PPN, $m = 5$) and poly(hexamethylene 2,6-naphthalate) (PHN, $m = 6$) [11–13], and found that PPN has one triclinic crystal structure and PHN has two crystal structures, α-form and β-form, depending upon the crystallization temperature. The pentamethylene unit of PPN backbone in its unit cell is in *gauche/gauche* conformation [11], whereas the hexamethylene units in both crystal structures of PHN are nearly in all-*trans* conformation [12,13].

It has recently been recognized that poly(trimethylene 2,6-naphthalate) (PTN, $m = 3$) has a high potential to be used for an engineering plastic. Accordingly, polymerization kinetics, characterization, rheological, and thermal properties of PTN have been extensively studied [14–18]. For instance, we have recently studied the crystallization and melting behavior of PTN and found that PTN has two different crystal structures, α-form and β-form, depending upon the crystallization temperature [19]. However, the crystal structures of PTN have not been completely

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* Corresponding authors. Tel.: 82-2-880-7192; fax: 82-2-885-1748.
E-mail address: whjpoly@plaza.snu.ac.kr (W.H. Jo).
Tel.: +82-54-467-4296; fax: +82-54-467-4050
E-mail address: leesc@knut.kumoh.ac.kr (S.C. Lee)

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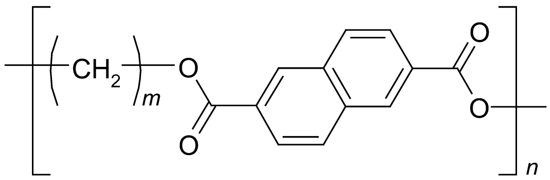


Fig. 1. Chemical structure of poly(*m*-methylene 2,6-naphthalate).

identified yet. Therefore, the crystal structure and chain conformation of the PTN β-form crystal are identified in the present study using X-ray powder diffraction and molecular modeling.

2. Experimental

2.1. Materials

PTN used in this study was prepared by melt-condensation reaction of 1,3-propandiol with dimethyl-2,6-naphthalate using tetraisopropyl orthotitanate as a catalyst. The synthesis and characterization of PTN are well described in Ref. [19]. In order to obtain an X-ray powder diffractogram for the pure β-form crystal of PTN, fine powder was prepared by the solution/precipitation method and then annealed at 205 °C for 24 h under nitrogen gas purging to minimize the oxidative degradation.

2.2. X-ray diffraction

The X-ray powder diffractogram of the annealed powder sample was recorded on a M18XHF diffractometer (MAC Science Co.) operating at 50 kV and 100 mA with Ni-filtered Cu Kα radiation. The diffractometer was equipped with a $2\theta/\theta$ goniometer, a divergence slit (1.0°), a scattering slit (1.0°), and a receiving slit (0.30 mm). The X-ray powder diffractograms were recorded at room temperature. The range of 2θ diffraction angle examined was 5–40°, the count time for each step was equal to 5 s/step, and the step width was 0.05° (2θ). The sample-to-detector distance or *d*-spacing was calibrated using Si powder ($2\theta = 28.44°$) as a standard. We have checked to minimize the preferred orientation of crystallites in the powder sample.

2.3. Molecular modeling

Conformational analysis, crystal structure modeling, and simulation of the X-ray powder pattern were carried out with the aid of molecular mechanics calculation using a commercial software Cerius^2 (version 4.0, Molecular Simulation Inc.) on a Silicon Graphics Indigo II workstation. The total potential energy of a molecular chain consists of contributions from intramolecular and intermolecular interactions. The intramolecular interactions consist of the bond stretching, valence angle bending, torsional, and inversion terms. The intermolecular interactions consist of van der Waals and Coulomb terms. The COMPASS force field [20] was used to calculate the potential energy of crystal structure, and the Ewald summation method was used in energy-minimizing calculations [21,22]. Standard bond lengths and angles for polyesters were adopted to build the repeating unit.

To obtain the useful conformational information of PTN such as local structure and chain flexibility, the conformational grid search is performed by varying simultaneously the torsional angles of successive bonds and by plotting the total energy against each pair of rotational angles. In the grid scan method, the potential energy is calculated whenever a specific torsional angle is varied over a grid of an equally spaced value. When the rotations of two successive bonds are considered, the torsional angle of the first bond is fixed at a given value and then the potential energies are calculated while the torsional angle of the second bond is varied. For the conformational grid search, only one repeat unit of PTN is considered, since we are only concerned with energies associated with torsional rotations of particular bonds.

In modeling of the crystal structure of PTN, the length of repeating unit was adjusted to match it with the experimental *c*-axis. The chain was then translated and rotated within the unit cell in order to minimize the packing energy. During the energy minimization, the unit cell parameters were kept constant. The modeled structure factors ($|F_{\mathrm{mod}}|$) were calculated using the atomic coordinates corresponding to the energy-minimized conformation of the chain in the unit cell. The intensity of a simulated X-ray diffraction pattern is expressed as:

$$I = ALp|F_{\mathrm{mod}}|^2 \exp(-2B_{\mathrm{iso}} \sin^2\theta/\lambda^2)$$

where A, L, p, $|F_{\mathrm{mod}}|$, and B_{iso} are the X-ray absorption coefficient of the sample, the Lorentz factor, the polarization factor, the modeled structure factor, and the isotropic temperature factor, respectively. The scale factor and overall isotropic temperature factor were refined to minimize the difference between the observed intensity (y_i(obs)) at the *i*th step and the calculated intensity (y_i(cal)). The reasonability of the final crystal structure was evaluated by using the following reliability factor (R_{p}) :

$$R_{\mathrm{p}} \frac{\sum|y_i(\mathrm{obs}) - y_i(\mathrm{cal})|}{\sum y_i(\mathrm{obs})} \times 100\%$$

3. Results and discussion

When monofilaments of PTN are uniaxially oriented and annealed at various temperatures to be used for the X-ray fiber diffraction pattern of the PTN β-form crystal, it was found that only α-form crystals are developed in the monofilaments irrespective of the annealing temperature. Consequently, we are not able to obtain the X-ray fiber diagram of the β-form crystal. Therefore, the X-ray powder diffraction pattern was used instead of the X-ray fiber diffraction to determine unit cell parameters of PTN β-form crystal by a trial and error method. Then, the procedure was further refined by a least-square procedure. The triclinic unit cell dimensions thus determined are listed in Table 1. From comparison between the measured crystal density and the calculated one, it is expected that one polymer chain with two chemical repeating repeat units passes through the unit cell along the *c*-axis. Table 1 also shows that the crystallographic repeat length of 2.218 nm is shorter than the length of two chemical repeat units (2.926 nm) of the fully extended conformation of PTN backbone, which indicates that the trimethylene sequences in the unit cell are not in fully extended conformation.

The chemical structure of two repeat units of PTN is shown in Fig. 2, where the numbering of the atoms and torsion angles are designated. Contour maps of conformational energy with respect to the torsional angles of successive bonds (ϕ_1 vs. ϕ_2, ϕ_2 vs. ϕ_3, ϕ_3 vs. ϕ_4 and ϕ_4 vs. ϕ_5) were calculated and shown in Fig. 3, from which various molecular models of PTN satisfying the crystallographic repeat length of *c*-axis (fiber axis) were first generated in the unit cell. Then, the total energy of the unit cell was minimized by molecular mechanics calculation. Since the carboxylic groups in aromatic polyesters are nearly coplanar to the aromatic ring plane, as verified from the contour maps (ϕ_1 vs. ϕ_2 and ϕ_2 vs. ϕ_3) of Fig. 3, several molecular models were chosen by varying the torsional angles of ϕ_3, ϕ_4, ϕ_5 and ϕ_6. Finally, when the total energies of such molecular models are compared with each other, it was found that a structural model with the *gauche*/*gauche* conformation in the middle part of trimethylene unit has the minimum energy. When the experimental X-ray powder diffraction intensity profile is compared with the one simulated from the energy-minimized crystal structure, it reveals that two diffraction intensity profiles are nearly identical, as shown in Fig. 4. The reliability factor thus obtained was $R_p = 4.4\%$. The overall isotropic temperature factor was estimated to be 5.0 Å^2. The bond lengths and bond angles of the final structural model are listed in Table 2. The torsion angles of trimethylene group in the unit cell of β-form crystal are determined to be $\phi_1 = -\phi'_1 = -179.0°$, $\phi_2 = -\phi'_2 = 178.9°$, $\phi_3 = -\phi'_3 = 170.5°$, $\phi_4 = -\phi'_4 = 66.6°$, $\phi_5 = -\phi'_5 = 58.1°$, $\phi_6 = -\phi'_6 = 157.1°$, $\phi_7 = -\phi'_7 = 175.6°$, and $\phi_8 = -\phi'_8 = 179.0°$. These results indicate that the midpoints of two naphthalene units in the unit cell of β-form crystal are crystallographic centers of symmetry along *c*-axis and that trimethylene sequences are in *gauche*/*gauche* conformation. Fractional coordinates of each atom in the β-form unit cell are listed in Table 3, and the molecular packing of PTN chain in the unit cell is shown in Fig. 5. The molecular packing demonstrates that the carboxylic groups in PTN are nearly coplanar to the naphthalene ring plane and that successive naphthaloyl groups are inclined to the crystal *c*-axis by the opposite direction, forming π-stacks that favor the lowest energy of the unit cell. This Z-shaped arrangement of chain backbone in the PTN β-form crystal is also observed in the crystal of poly(trimethylene terephthalate) [23,24].

Table 1
Crystallographic data of PTN β-form crystal

Crystal system	Triclinic
Space group	$P\bar{1}$
Cell parameters	
a (nm)	0.4665
b (nm)	0.7014
c (nm)	2.2177
α (°)	100.85
β (°)	88.78
γ (°)	120.63
Repeating units/unit cell	2
Calculated density (g cm^{-3})	1.393
Observed density (g cm^{-3})	1.37

Table 2
Bond lengths and bond angles in the PTN β-form crystal

Bond length		Bond angle	
Bond	Length (nm)	Bonds	Angle (°)
C1–C2	0.1403	C1–C2–C3	121.3
C1–C4	0.1387	C1–C4–C5	121.4
C1–C6	0.1481	C1–C6–O2	112.8
C2–C3	0.1378	C2–C1–C4	119.4
C3–C5′	0.1417	C2–C1–C6	121.4
C4–C5	0.1410	C2–C3–C4	120.0
C5–C5′	0.1442	C3–C5′–C5	118.6
C6–O1	0.1212	C4–C5–C5′	118.8
C6–O2	0.1367	C6–O2–C7	117.8
O2–C7	0.1444	O2–C7–C8	107.5
C7–C8	0.1525	C7–C8–C9	116.9
C8–C9	0.1531	C8–C9–C10	117.5
C9–C10	0.1534	C9–C10–C11	114.2
C10–C11	0.1527	C10–C11–O3	109.9
C11–O3	0.1443	C11–O3–C12	117.1
O3–C12	0.1369	O3–C12–C13	112.6
C12–O4	0.1213	C12–C13–C14	121.2
C12–C13	0.1482	C13–C14–C15	121.4
C13–C14	0.1403	C13–C16–C17	121.3
C13–C16	0.1387	C14–C13–C16	119.3
C14–C15	0.1378	C14–C15–C17′	120.6
C15–C17′	0.1417	C15–C17′–C17	118.5
C16–C17	0.1410	C16–C17–C17′	118.9
C17–C17′	0.1442		

4. Conclusions

We have recently found that poly(trimethylene 2,6-naphthalate) (PTN) has two crystal structures, α- and β-form, depending upon the crystallization temperature. In this study, the crystal structure of PTN β-form crystal, developed at high crystallization temperatures, is successfully

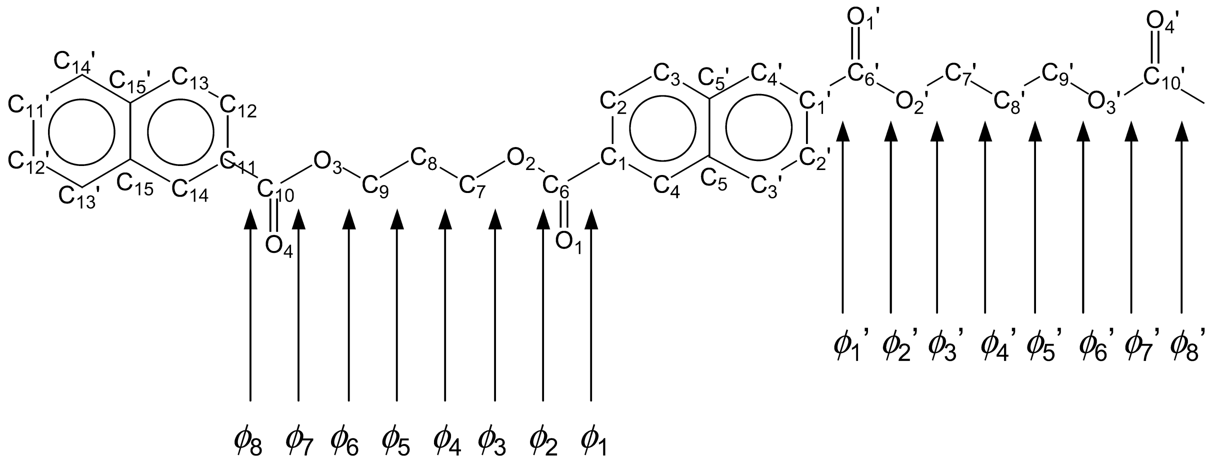


Fig. 2. Numbering of atoms and torsional angles in the repeat unit of PTN.

identified by using the X-ray powder diffraction combined with the molecular modeling technique. The unit cell of PTN β-form crystal was found to be triclinic ($P\bar{1}$ space group) with dimensions of $a = 0.4665$ nm, $b = 0.7014$ nm, $c = 2.2177$ nm, $\alpha = 100.85°$, $\beta = 88.78°$, and $\gamma = 120.63°$. The observed crystal density of 1.37 g cm^{-3} and the determined dimensions of unit cell indicate that the unit cell contains one polymer chain with two repeating units. In the unit cell, each trimethylene unit in PTN backbone is in *gauche*/*gauche* conformation and the neighboring naphthalene units are in face-to-face type arrangement. Since we have recently identified that the PTN α-form crystal is monoclinic with unit cell parameters of $a = 0.722$ nm, $b = 0.709$ nm, $c = 2.384$ nm, $\alpha = 90.0°$,

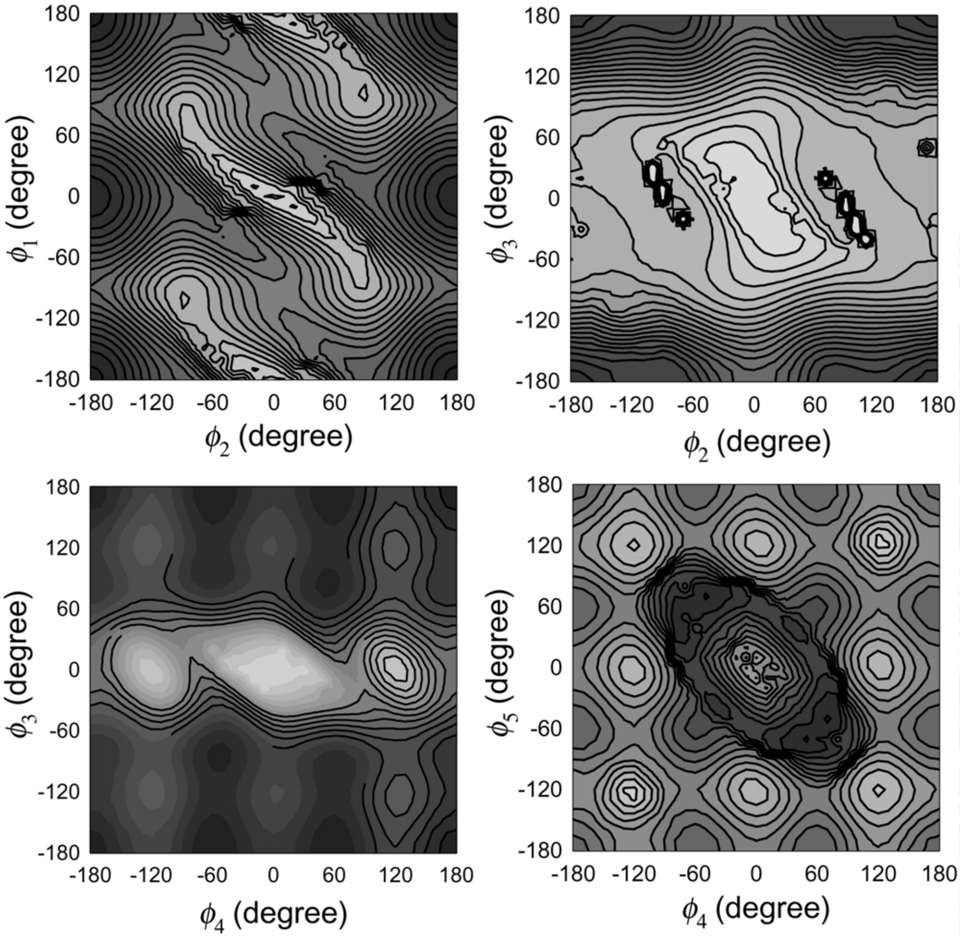


Fig. 3. Contour maps of conformational energy calculated for each pair of dihedral angles of PTN backbone shown in Fig. 2. Energy contour lines are drawn every 1 kcal mol^{-1} and the darker region indicates the lower energy level.

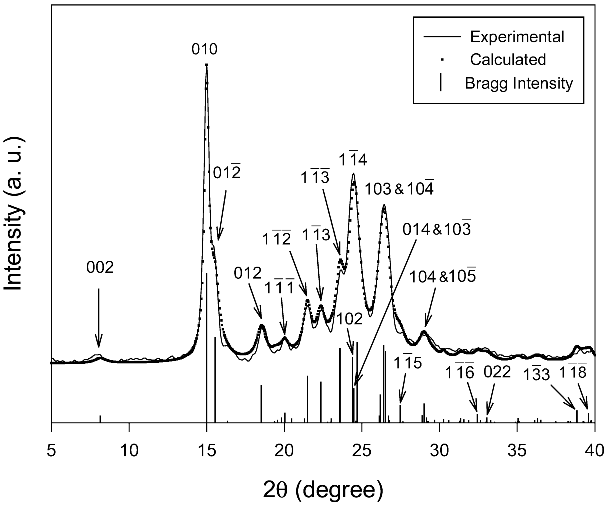
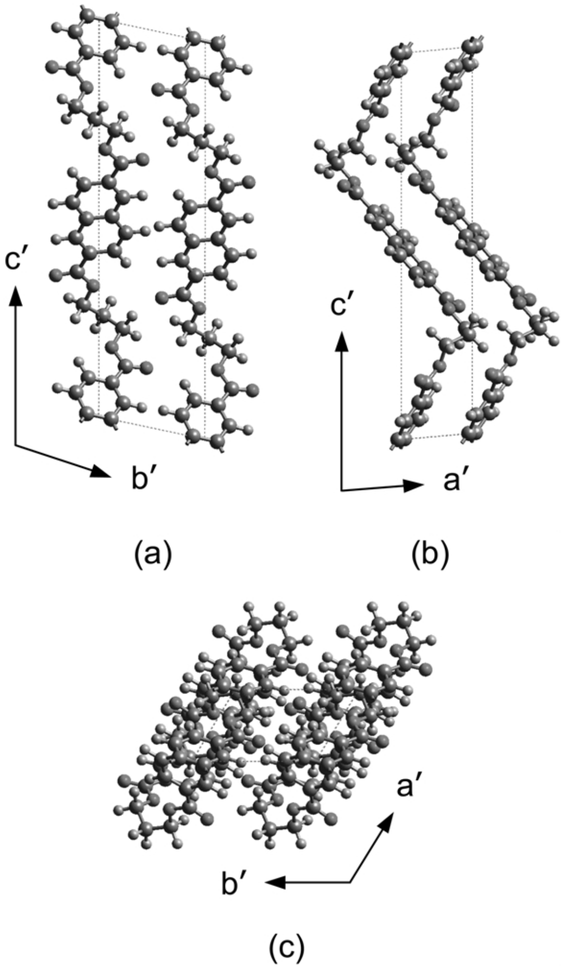


Fig. 4. Comparison of the experimental X-ray powder diffraction intensity profile of PTN β-form crystal with the simulated one. The sample for powder diffraction intensity profile was annealed at 205 °C. The amorphous contribution has already been subtracted from the experimental X-ray powder diffraction.

Table 3
Fractional atomic coordinates in the PTN β-form crystal

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C1	−0.3829	−0.0909	0.4066
C2	−0.2061	0.1457	0.4262
C3	0.0265	0.2509	0.4767
C4	−0.3183	−0.2199	0.4381
C5	−0.0880	−0.1195	0.4908
C6	−0.6369	−0.2056	0.3529
C7	−0.9050	−0.1483	0.2727
C8	−0.9473	0.0383	0.2563
C9	−0.6337	0.2231	0.2343
C10	−0.3483	0.2508	0.1408
C11	−0.2488	0.1242	0.0923
C12	−0.3396	−0.1000	0.0921
C13	−0.2393	−0.2161	0.0482
C14	−0.0585	0.2294	0.0468
C15	0.0468	0.1165	0.0006
O1	−0.8075	−0.4078	0.3323
O2	−0.6687	−0.0561	0.3261
O3	−0.5397	0.1206	0.1812
O4	−0.2758	0.4465	0.1478
H2	−0.2476	0.2531	0.4016
H3	0.1645	0.4361	0.4911
H4	−0.4479	−0.4050	0.4227
H7	−0.1890	−0.2234	0.2337
H7′	−0.1481	−0.2856	0.2822
H8	−0.0225	0.1137	0.2970
H8′	−0.1526	−0.0366	0.2196
H9	−0.4266	0.3122	0.2710
H9′	−0.6842	0.3499	0.2228
H12	−0.4921	−0.1898	0.1271
H13	−0.3106	−0.3904	0.0499
H14	0.0155	0.4048	0.0458

H7 and H7′ mean hydrogens which are covalent-bonded to C7.



(a) (b)

(c)

Fig. 5. Molecular packing of PTN backbone in the unit cell of β-form crystal: (a) projection along *a*-axis; (b) projection along *b*-axis; (c) projection along *c*-axis.

$\beta = 90.0°$, and $\gamma = 81.6°$, the detailed crystal structure and chain conformation of PTN α-form and the mechanism of crystal transformation from α-form to β-form and vice versa will be reported in near future.

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