

Conformation and Packing of Odd-Numbered α -Oligothiophenes in Single Crystals

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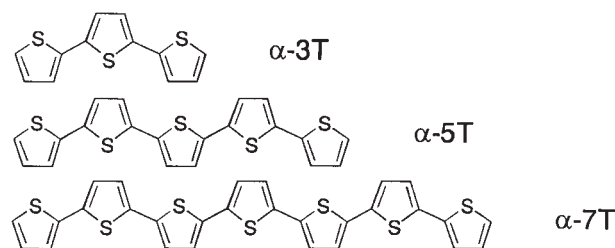
X-ray single crystal analyses revealed the molecular geometry and molecular packing of odd-numbered α -oligothiophenes (septhiophene, quinquethiophene and terthiophene) in single crystals prepared by sublimation. Sепthiophene crystallizes into triclinic, which is in contrast to the monoclinic packing of even-numbered oligomers. The molecular arrangement of septhiophene in a single crystal resembles that reported for even-numbered oligomers, while the molecules take a more random conformation: only one of the two terminal thienyl rings exhibits disorder and significant torsion from the conjugated plane. The X-ray diffraction data of a quinquethiophene single crystal suggest that the molecule with one of the two different orientations randomly occupies each site.

Organic semiconducting compounds consisting of conjugated oligomers and polymers have been studied as promising materials for electronic and optoelectronic devices.^{1–4} Because they possess features different from those of inorganic materials, they offer potential materials not only as replacements of conventional inorganic materials, but also for completely different types of devices. A great deal of effort has been made to improve the efficiencies and stabilities of these materials.

Oligothiophenes and polythiophenes are good candidates for applications because of their excellent electronic properties, stability under ambient conditions, and ease of chemical modification.¹ Recently, oligothiophenes with defined conjugation lengths have received much attention as model compounds to obtain a better understanding of the structure-physical properties relationship.^{1,2,4} The molecular conformation and molecular packing are indispensable information since these materials are in most cases expected to be used in the solid state.

Unsubstituted α -oligothiophenes, the simplest compounds in the family, have been intensively studied since Horowitz et al. demonstrated the high charge mobility of α -sexithiophene (α -6T).⁵ Although unsubstituted α -oligothiophenes have poor solubility in organic solvents, which renders the application of wet fabrication processes difficult, their thin films are easily evaporated onto solid surfaces.

So far, the crystal structures of α -bithiophene (α -2T), terthiophene (3T), quaterthiophene (4T), 6T and octithiophene (8T) have been solved using single crystals.^{6–13} They display quite anisotropic packing with all the long molecular axes parallel to one another. As for quinquethiophene (5T), the crystal



Scheme 1.

structure was reported only for powder samples using Riedveld method.¹⁴ It is therefore indispensable to examine the molecular packing of 5T and septhiophene (7T) in single crystals (Scheme 1). Furthermore interest arises from the analogy of “even-odd effect” of crystal packing of paraffins. It has been known that the molecular packing of *n*-alkanes, fatty acids, liquid crystals and long-chain amphiphiles depends strongly on the parity of the number of carbon atoms in the methylene chains, which affects their physical properties, such as the melting point.^{15–20} Since a thiophene ring is five-membered, the direction of the bond between two thiophene rings has a finite angle with respect to the long axis of the oligothiophene molecule. This feature, similar to that of methylene chains of paraffins, will cause the dependence of the molecular packing of oligothiophenes on the parity of the number of thiophene rings. In this paper we show the molecular geometry and molecular packing of odd-numbered oligothiophenes in single crystals prepared by sublimation.

Experimental

Materials. 1,3-Bis(diphenylphosphino)propane nickel(II) chloride ($\text{NiCl}_2(\text{dppp})$) was purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received. Other reagents and solvents were purchased from Wako Chemicals Co. and used as received. 2-Bromobithiophene, 2,5''-dibromoterthiophene, 2,2':5',2''-terthiophene (α -3T), 2,2':5',2'':5'',2''':5''',2''''-quinquethiophene (α -5T), were synthesized following the reported method.^{21–23}

2,2':5',2'':5'',2''':5''',2''''-Septithiophene (α -7T): A solution of 2-bromobithiophene (3.0 g, 12.2 mmol) in dried diethyl ether (10 mL) was added dropwise to magnesium turnings (0.29 g, 12.2 mmol) in boiling diethyl ether (2 mL). The resulting mixture was refluxed for 2 hrs, allowed to cool to room temperature, and transferred with a syringe to the dropping funnel of a second apparatus. The Grignard solution was added dropwise to a solution of 2,5''-dibromoterthiophene (2.3 g, 5.6 mmol) and $\text{NiCl}_2(\text{dppp})$ (30.3 mg, 56 μmol) in a 1:1 mixture of dried benzene and diethyl ether (20 mL). The resulting red dispersion was refluxed for 6 hrs, allowed to cool to room temperature, and hydrolyzed with ice cold 1 M HCl. The precipitate was filtered, washed repeatedly with a diluted HCl solution and water, and dried in vacuo. After Soxhlet extraction with hexane, the remaining powder was repeatedly sublimed to obtain red crystals. Yield: 0.32 g (9.9%). mp 344–346 °C (Lit. mp 327–328 °C²⁴). Anal. Found: C, 58.30; H, 2.33; S, 38.71%. Calcd. For $\text{C}_{28}\text{H}_{16}\text{S}_7$: C, 58.30; H, 2.79; S, 38.91%.

Single crystals of α -7T were obtained by sublimation with a slight modification of the method reported by others (Fig. 1).^{9–11,13,25} A compound of 50–150 mg was placed at the bottom of a glass tube of 15 mm in diameter. Nitrogen was introduced through an inner glass tube whose edge was positioned ca. 10 mm above the bottom of the outer tube. The bottom of the

outer tube was heated at 340–380 °C under a reduced pressure of nitrogen (ca. 7 hPa) for several hours.

α -5T crystals were obtained by heating at 240–250 °C under reduced pressure of nitrogen using a similar apparatus as in the case of α -7T. Crystals of α -3T were prepared using an ordinary sublimation apparatus by heating at ca. 95 °C under reduced pressure.

X-ray Crystal Structure Analyses. α -7T Crystal at 206 K: Red plate, $0.33 \times 0.20 \times 0.03$ mm. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. $\mu(\text{Cu } K\alpha) = 60.90 \text{ cm}^{-1}$. Reflections measured: 10534, unique: 9271, of which 6297 had $I > 2\sigma(I)$. No decay correction. An empirical absorption correction was applied. A structure determination was done using the teXsan crystallographic software package²⁶ with direct methods using SIR92 and refinements with full-matrix least-squares on F^2 for 631 variable parameters. All non-hydrogen atoms were refined anisotropically. Twenty five hydrogen atoms out of 32 were found in the difference Fourier map and others were attached at calculated positions. $R1 = 0.097$ ($I > 2\sigma(I)$), $Rw^2 = 0.270$ ($I > 0\sigma(I)$), residual electron density $+0.86/-0.79 \text{ e}\text{\AA}^{-3}$. The graphics were performed using PLATON.²⁷ Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-192275.

α -7T Crystal at Room Temperature: Red disc, $0.25 \times 0.25 \times 0.06$ mm. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. $\mu(\text{Cu } K\alpha) = 60.28 \text{ cm}^{-1}$. Reflections measured: 9121, unique: 8935, of which 5862 had $I > 2\sigma(I)$. No decay correction. An empirical absorption correction was applied. A structure determination was done using the teXsan crystallographic software package with direct methods using SIR92 and refinements with full-matrix least-squares on F for 631 variable parameters. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were attached at calculated positions. $R = 0.102$, $R_w = 0.156$, residual electron density $+0.54/-0.51 \text{ e}\text{\AA}^{-3}$. The crystal structure of α -7T at room temperature is essentially the same as that obtained at 206 K, suggesting no phase transition. Triclinic $P\bar{1}$, $a = 5.988(1) \text{ \AA}$, $b = 7.823(2) \text{ \AA}$, $c = 52.865(9) \text{ \AA}$, $\alpha = 91.16(2)^\circ$, $\beta = 91.50(1)^\circ$, $\gamma = 89.94(2)^\circ$, $Z = 4$.

α -5T Crystal: Orange plate, $0.40 \times 0.26 \times 0.10$ mm. Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. $\mu(\text{Cu } K\alpha) = 58.70 \text{ cm}^{-1}$. Reflections measured: 3010, unique: 1459, of which 488 had $I > 4\sigma(I)$. No decay correction. An empirical absorption correction was applied. A structure determination was done using the teXsan crystallographic software package with direct methods using SIR92 and refinements with full-matrix least-squares on F for 101 variable parameters. All non-hydrogen atoms were refined isotropically. Hydrogen atoms were not included. $R = 0.203$, $R_w = 0.162$, residual electron density $+0.43/-0.49 \text{ e}\text{\AA}^{-3}$.

α -3T Crystal: Yellow plate, $0.60 \times 0.20 \times 0.05$ mm. RIGAKU AFC7R diffractometer at 203 K using graphite-monochromated Mo $K\alpha$ radiation. $\mu(\text{Mo } K\alpha) = 6.23 \text{ cm}^{-1}$. Reflections measured: 10336, unique: 5166, of which 3212 had $I > 3\sigma(I)$. No decay correction. An empirical absorption correction was applied. A structure determination was done using the teXsan crystallographic software package with direct methods using SIR92 and refinements with full-matrix least-squares on F for 271 variable parameters. All non-hydrogen atoms were refined anisotropically. $R = 0.057$, $R_w = 0.078$, residual electron density $+0.15/-0.17 \text{ e}\text{\AA}^{-3}$.

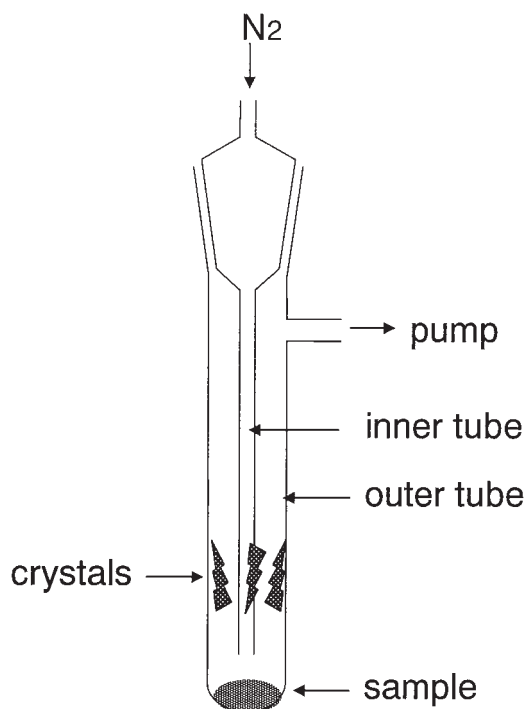


Fig. 1. Apparatus for sublimation.

Results and Discussion

All three compounds (α -3T, 5T and 7T) formed crystals large enough for X-ray analysis. The crystal structure of α -3T in the crystal formed by sublimation was essentially the same as that in the crystal fabricated by re-crystallization from an ether solution.⁸ Because the packing manner of 3T is significantly different from those of larger oligomers, probably due to the lack of molecular length, 3T was not included in the discussion.

Red, shell-like crystals with sizes up to 2 mm in diameter and 0.1 mm in thickness were formed by sublimation of α -7T. The X-ray diffraction was measured both at room temperature and at low temperature (206 K). The molecular structure of α -7T in a single crystal with atomic numbering scheme obtained from the measurement at 206 K is shown in Fig. 2a. Crystal data are collected in Table 1. There are two crystallographically independent molecules in an asymmetric unit whose conformation is similar to each other. This is in contrast to the results for the oligomers with even thiophene rings, such as α -4T (low-temperature polymorph),⁹ 6T (low-temperature polymorph)¹¹ and 8T,¹³ where there is only one crystallographically independent molecule. The molecules exhibit an approximately flat conformation. The terminal thienyl rings at

Table 1. Structure Determination Summary

	7T	5T ^{a)}	3T ^{b)}
Formula	C ₂₈ H ₁₆ S ₇	C ₂₀ H ₁₂ S ₅	C ₁₂ H ₈ S ₃
Formula weight	576.90	412.65	248.39
Temperature/K	206	296	203
Crystal system	triclinic	(monoclinic)	monoclinic
Space group	<i>P</i> $\bar{1}$	(<i>P</i> 2 ₁ / <i>a</i>)	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	5.953(1)	(6.014(1))	15.349(1)
<i>b</i> /Å	7.767(1)	(7.766(1))	5.688(1)
<i>c</i> /Å	53.02(1)	(19.611(3))	25.80(1)
α /°	91.21(1)	(90)	90
β /°	91.89(1)	(97.70(1))	97.883(4)
γ /°	89.92(1)	(90)	90
<i>V</i> /Å ³	2449.6(6)	(907.7(2))	2331.1(9)
<i>Z</i>	4	(2)	8
$\rho_{\text{calcd}}/\text{Mg m}^{-3}$	1.564(1.548 ^{c)})	1.510	1.479

a) α -5T has significant disorder in a crystal (see the text). Further analyses were therefore not successful. b) The crystal structure of α -3T was essentially same as that in the crystal fabricated by re-crystallization from an ether solution.⁸ c) Calculated density based on the measurements at room temperature.

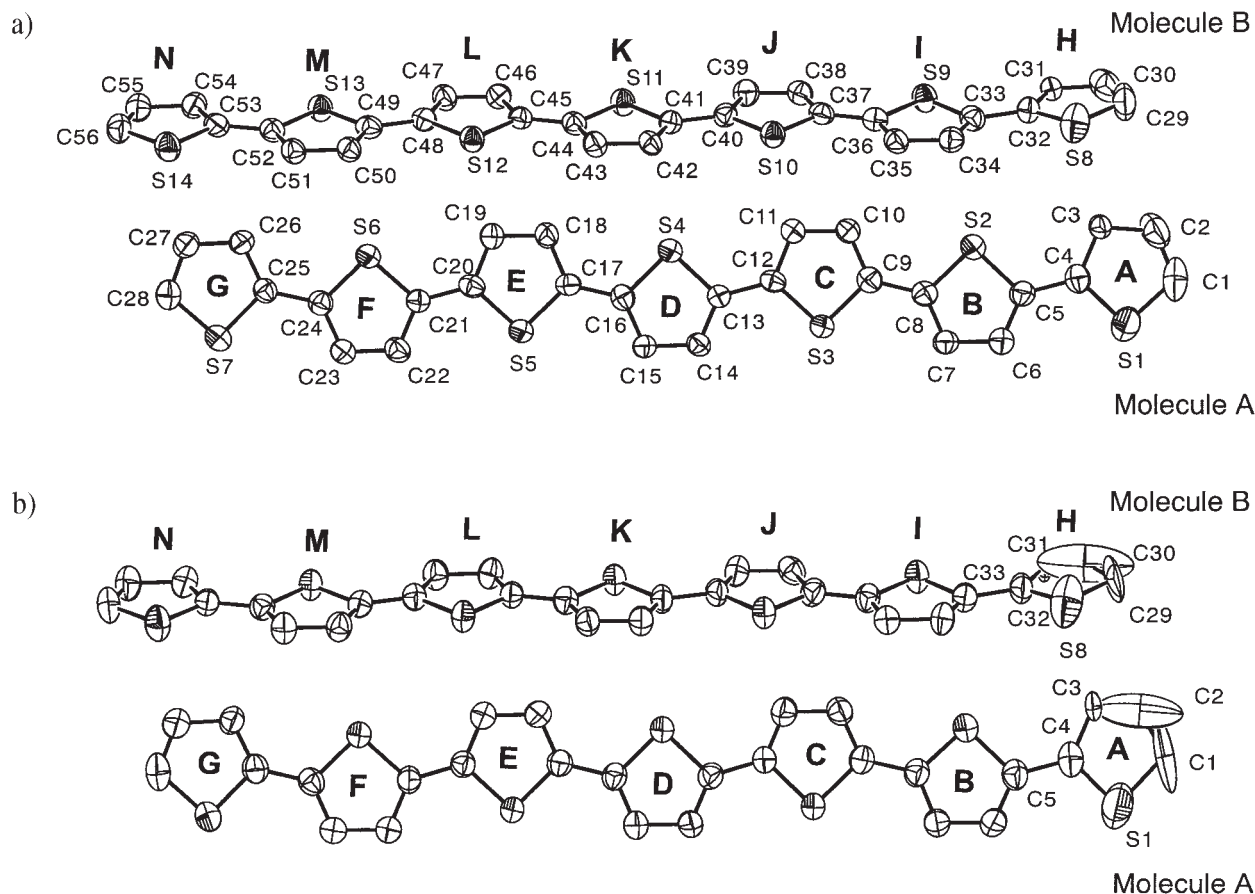


Fig. 2. a) Molecular structure of α -7T with the atomic numbering scheme obtained by the measurements at 206 K. Displacement ellipsoids are drawn at the 50% probability level. Torsion angles between adjacent thiophene rings: A–B 7.1(4)°, B–C 0.7(3)°, C–D 0.6(3)°, D–E 0.5(3)°, E–F 0.6(3)°, F–G 1.9(3)°, H–I 6.6(4)°, I–J 0.5(3)°, J–K 0.2(3)°, K–L 0.6(3)°, L–M 0.6(3)°, M–N 1.1(3)°. b) Molecular structure of α -7T obtained by the measurements at room temperature. Large disorder is observed only at rings A and H, and not at rings G or N.

one of the edges of the molecule, rings A and H in Fig. 2a, however, twist significantly along the C4–C5 and C32–C33 bonds. The dihedral angle between rings A and B is $7.1(4)^\circ$, the one between H and I is $6.6(4)^\circ$, and the others are less than 2.0° . Moreover, the π -conjugating plane of the molecules is bent at rings A and H. Such a significant torsion and a bend of the molecules have not been observed for even-numbered oligothiophenes.^{9,11,13}

The thiophene rings of 7T have essentially been revealed to take an all-*anti* conformation. Disorder is suggested at rings A and H by relatively large bond lengths at C(3)–C(4) (1.440(8) Å) and C(31)–C(32) (1.422(8) Å) compared with the other C=C double bonds in the molecules (1.32–1.40 Å, Table 2). The bond lengths at S(1)–C(4) (1.702(7) Å) and S(8)–C(32) (1.699(7) Å) also deviate from the normal value of the S–C bond lengths. The X-ray data taken at room temperature show greater disorder (Fig. 2b). The bond lengths and angles at rings A and H deviate significantly from the normal values for a thiophene ring, and the atoms have large temperature factors. The feature should arise from the large mobility of rings A and H. The contribution of a small fraction of sulfur at positions C(3) and C(31) due to the random coexistence of *syn* and *anti* conformations is also suspected. A similar elongation of C=C double bonds at terminal thienyl rings, although to a lesser extent, are seen for 2T,⁷ 3T,⁸ 4T (high-temperature polymorph)^{9,10} and 6T (high-temperature poly-

morph),¹² while this feature is not always mentioned explicitly in the literature. What is intriguing is that the disorder takes place only at one edge of the molecule in the present case, i.e., at rings A and H, and not at ring G or N. Disorder at only one edge of the molecule is not common in the crystals of oligothiophene derivatives, but has been reported for a substituted quinquethiophene (5T) derivative.²⁸ Thus, this feature seems to be related to the parity of the number of thiophene units.

α -7T was crystallized in triclinic, $P\bar{1}$, which is in contrast to the monoclinic packing of α -4T (low-temperature polymorph),⁹ 6T (low-temperature polymorph)¹¹ and 8T.¹³ This may be related to the less symmetric shape of α -7T compared with those of even-numbered oligomers. The angles α ($91.21(1)^\circ$) and γ ($89.92(1)^\circ$), however, deviate only slightly from 90° . The deviation of the packing manner of α -7T from the monoclinic one is thus small.

Figure 3 shows packing diagrams of α -6T, 7T and 8T.²⁹ α -7T molecules are packed in a manner similar to α -6T and 8T. The lengths of two shorter axes ($a = 5.953(1)$ Å, $b = 7.767(1)$ Å) are nearly identical to those for even-numbered oligomers. The length of the longest axis ($c = 53.02(1)$ Å) is between those for α -6T (low-temperature polymorph) and 8T. 7T molecules take herringbone-like arrangement. The angle between the planes of neighboring molecules is ca. 63° , which is slightly smaller than those of α -6T (low-temperature polymorph,

Table 2. Bond Lengths of α -7T Based on the Measurements at 206 K

C=C double bond (Å)			C–C single bond (thiophene ring) (Å)			S–C bond (Å)		
C(1)	C(2)	1.35(1)	C(2)	C(3)	1.386(9)	S(1)	C(1)	1.692(9)
C(3)	C(4)	1.440(8)	C(6)	C(7)	1.406(8)	S(1)	C(4)	1.702(7)
C(5)	C(6)	1.349(8)	C(10)	C(11)	1.415(8)	S(2)	C(5)	1.736(6)
C(7)	C(8)	1.383(8)	C(14)	C(15)	1.405(8)	S(2)	C(8)	1.724(6)
C(9)	C(10)	1.376(8)	C(18)	C(19)	1.410(8)	S(3)	C(9)	1.730(6)
C(11)	C(12)	1.380(8)	C(22)	C(23)	1.390(8)	S(3)	C(12)	1.729(6)
C(13)	C(14)	1.362(8)	C(26)	C(27)	1.407(8)	S(4)	C(13)	1.727(6)
C(15)	C(16)	1.395(8)	C(30)	C(31)	1.373(10)	S(4)	C(16)	1.722(6)
C(17)	C(18)	1.384(8)	C(34)	C(35)	1.404(8)	S(5)	C(17)	1.728(6)
C(19)	C(20)	1.392(8)	C(38)	C(39)	1.395(8)	S(5)	C(20)	1.724(6)
C(21)	C(22)	1.378(8)	C(42)	C(43)	1.420(8)	S(6)	C(21)	1.722(6)
C(23)	C(24)	1.389(8)	C(46)	C(47)	1.396(8)	S(6)	C(24)	1.721(6)
C(25)	C(26)	1.378(8)	C(50)	C(51)	1.415(8)	S(7)	C(25)	1.722(6)
C(27)	C(28)	1.369(9)	C(54)	C(55)	1.411(8)	S(7)	C(28)	1.686(7)
C(29)	C(30)	1.35(1)				S(8)	C(29)	1.692(10)
C(31)	C(32)	1.422(8)	C–C single bond (inter-ring) (Å)			S(8)	C(32)	1.699(7)
C(33)	C(34)	1.366(8)				S(9)	C(33)	1.717(7)
C(35)	C(36)	1.399(8)	C(4)	C(5)	1.456(8)	S(9)	C(36)	1.726(6)
C(37)	C(38)	1.365(8)	C(8)	C(9)	1.449(8)	S(10)	C(37)	1.744(6)
C(39)	C(40)	1.383(8)	C(12)	C(13)	1.450(8)	S(10)	C(40)	1.717(6)
C(41)	C(42)	1.356(8)	C(16)	C(17)	1.446(8)	S(11)	C(41)	1.725(6)
C(43)	C(44)	1.394(8)	C(20)	C(21)	1.444(8)	S(11)	C(44)	1.727(6)
C(45)	C(46)	1.379(8)	C(24)	C(25)	1.459(8)	S(12)	C(45)	1.738(6)
C(47)	C(48)	1.383(8)	C(32)	C(33)	1.478(8)	S(12)	C(48)	1.725(6)
C(49)	C(50)	1.359(8)	C(36)	C(37)	1.439(8)	S(13)	C(49)	1.723(6)
C(51)	C(52)	1.382(8)	C(40)	C(41)	1.466(7)	S(13)	C(52)	1.725(6)
C(53)	C(54)	1.377(9)	C(44)	C(45)	1.441(8)	S(14)	C(53)	1.723(6)
C(55)	C(56)	1.331(9)	C(48)	C(49)	1.459(8)	S(14)	C(56)	1.713(7)
			C(52)	C(53)	1.459(8)			

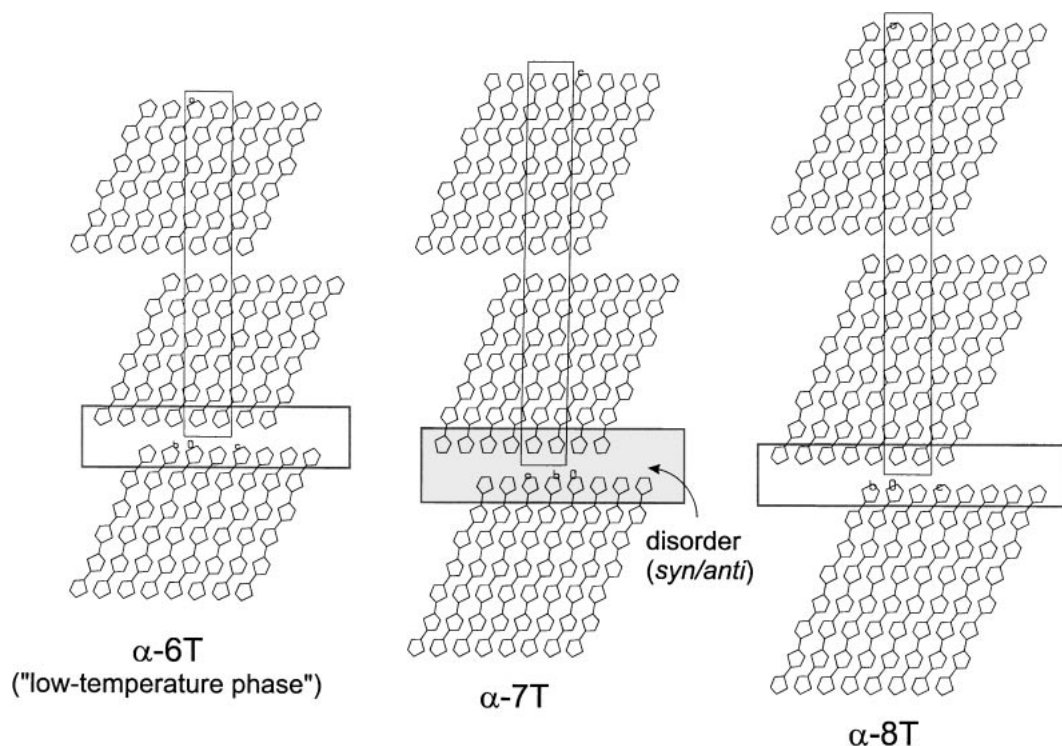


Fig. 3. Packing diagrams of α -6T, 7T and 8T. The diagrams of 6T and 8T are reproduced using the atomic coordination parameters reported in Refs. 11 and 13, respectively.

66°) and 8T (65°).¹³ The molecules exhibit layer-like packing with their long molecular axis slightly tilted from the normal of the *ab* plane. We assume the presence of "interfaces" between the molecular layers in the crystals.

A difference is found in the contacting manner between the nearest molecules at every two interfaces of the adjacent layers. At every interface of 6T and 8T, and at every two interfaces of 7T, only one of the C–H bonds of each terminal thieryl ring is directed toward the interface (Fig. 4a). Owing to the shape of the interface, the protruding C–H bonds of contacting layers are interdigitated. At the interface of 7T where the "disordered" terminal thieryl rings are located, two of the C–H bonds face the interface (Fig. 4b). The position of the molecules in the next layer is thus different from that in the former case, which causes the deviation from the monoclinic packing. Furthermore, the shape of the interface is smoother than that in the former case, which could lead to the less-defined manner of the conformation of the terminal thieryl rings in the adjacent layer.

The distances of less than 4 Å between the carbon atoms at two different interfaces of 7T are listed in Table 3. Carbon atoms at the "rough interface (corresponding to Fig. 4a)" exhibit more close interactions than those at the "smooth interface (corresponding to Fig. 4b)."

The above results suggest that the interaction between terminal rings of neighboring molecules is somewhat weaker for α -7T than for 6T and 8T. This feature seems to be reflected in the density of the crystal. Figure 5 shows the densities of α -oligothiophene crystals estimated from the lattice constants. The calculated density of the α -7T crystal based on room temperature measurements (1.548 g cm⁻³)³⁰ is smaller than those

Table 3. Distances Less than 4.0 Å between Terminal Carbon Atoms at Two Different Interfaces of α -7T Crystal

At the "rough interface" (Å) (corresponding to Fig. 4a)			At the "smooth interface" (Å) (corresponding to Fig. 4b)		
C(56)	C(56) ^{a)}	3.76(1)	C(2)	C(2) ^{b)}	3.69(2)
C(27)	C(55)	3.77(1)	C(30)	C(30) ^{c)}	3.72(2)
C(28)	C(28) ^{d)}	3.80(1)	C(1)	C(30) ^{e)}	3.89(1)
C(27)	C(56)	3.81(1)	C(2)	C(29)	3.93(1)
C(27)	C(55) ^{e)}	3.86(1)	C(2)	C(30)	3.99(1)
C(28)	C(56) ^{f)}	3.87(1)			
C(55)	C(56) ^{a)}	3.87(1)			
C(28)	C(55) ^{e)}	3.90(1)			

Symmetry code: a) $-1 - x, 1 - y, 1 - z$; b) $3 - x, -y, -z$; c) $2 - x, 1 - y, -z$; d) $-x, -y, 1 - z$; e) $1 + x, y, z$; f) $-x, 1 - y, 1 - z$.

reported for 6T (low-temperature polymorph, 1.553 g cm⁻³) and 8T (1.578 g cm⁻³).³¹

α -5T exhibits more disordered structures. Orange platelet crystals were obtained by sublimation of α -5T. Many of the crystals exhibit perfect extinction under crossed polarizers, indicating that they are single crystals. X-ray diffraction data, however, show that α -5T has large disorders in single crystals. We measured the diffractions of several single crystals, and found many different results for the lattice constants. The value of the longest crystal axis was sometimes too large considering the size of the molecule. The atomic coordination parameters of α -5T obtained by powder diffraction reported by Porzio et al.¹⁴ did not reproduce our diffraction data.

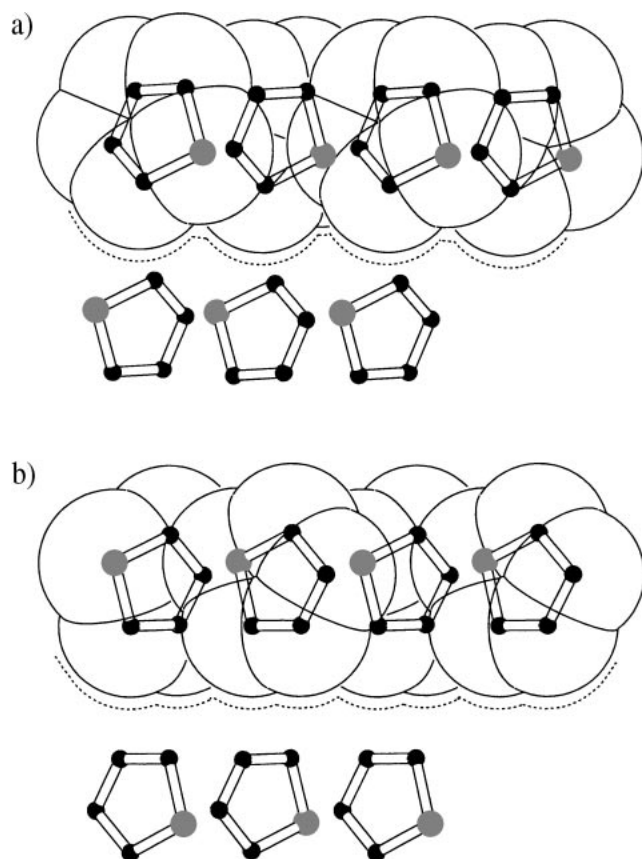


Fig. 4. a) Scheme of interface between molecular layers of α -6T, 8T and every two layers of 7T. Hydrogen atoms are omitted. The terminal thienyl rings of the molecules in the upper layer are illustrated with van der Waals radii. b) Scheme of interface between the molecular layers of 7T where "disordered" thienyl rings are located.

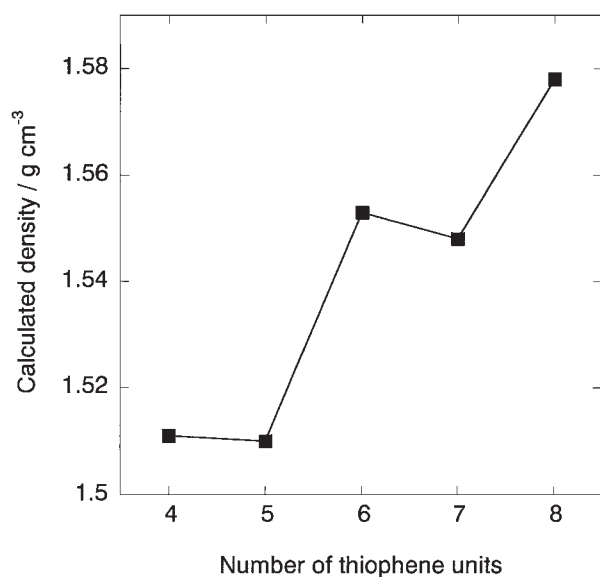


Fig. 5. Calculated densities of α -oligothiophene crystals. The values for α -4T, 6T and 8T are those reported in Refs. 9, 11 and 13, respectively.

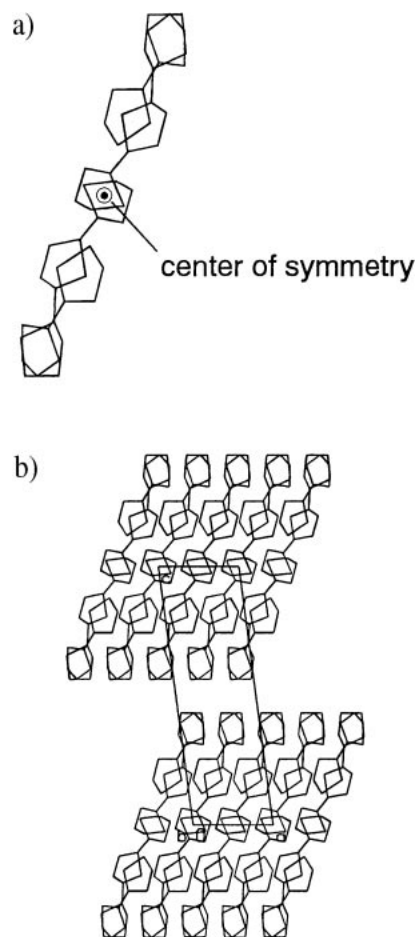


Fig. 6. a) Molecular structure of α -5T in one of the single crystals. Extinction rule and electron density map suggest that the molecule has inversion symmetry, which is impossible for α -5T. b) Packing diagram of α -5T in a single crystal.

The most successful results, but not enough for complete X-ray analysis, are shown below. The space group and the lattice constants obtained were $P2_1/a$, $a = 6.014(1)$ Å, $b = 7.766(1)$ Å, $c = 19.611(3)$ Å, $\beta = 97.70(1)^\circ$.³² The electron density map shows two overlapping quinquethiophene-like molecules which can be transformed to each other by inversion around the center of symmetry located in the middle of the molecule (Fig. 6a). The results suggest that α -5T with one of the two different orientations randomly occupies each site. An attempt to determine the contributions of α -5T molecules with two different orientations based on the electron density map was not successful. Figure 6b shows the molecular packing of α -5T in a single crystal. The packing manner of α -5T in a single crystal is similar to those of α -7T and even-numbered oligothiophenes, as can be seen by a comparison with Fig. 3.

Similar to the case of α -7T, the calculated density of α -5T crystal (1.510 g cm^{-3}) is smaller than the value obtained by the interpolation of the densities of even-numbered oligothiophenes, as can be seen in Fig. 5. This fact also suggests a looser packing of the molecules, which may cause the disorder.

Conclusions

The molecular geometry and molecular packing of odd-numbered α -oligothiophenes (α -7T, 5T and 3T) in single crystals prepared by sublimation were investigated by X-ray single crystal analyses. The molecular arrangement of α -7T in a single crystal resembles that reported for even-numbered oligomers, while the molecules take a more random conformation: only one of the two terminal thienyl rings exhibits disorder and significant torsion from the conjugated plane. The triclinic packing of α -7T is also in contrast to the monoclinic one of even-numbered oligomers. The X-ray diffraction data of the α -5T single crystal suggest that the molecule with one of the two different orientations randomly occupies each site.

The disorder seems to be reflected in the relatively small densities of the α -7T and 5T crystal compared with those of even-numbered oligomers. The above results show that an "even-odd effect" works not only for methylene chains, but also for five-membered aromatic compounds.

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- 29 The packing diagrams of α -6T (low-temperature polymorph) and 8T are reproduced using the atomic coordination parameters reported in Refs. 11 and 13, respectively.
- 30 As crystals shrink with decreasing the temperature, the value of calculated density for 7T obtained by the measurements at room temperature was employed for the comparison with those for the other oligomers.
- 31 Since estimated values of crystal densities depend on the condition of X-ray measurements, precise comparison of the density values of the crystals measured with different diffractometers is not appropriate. The smaller values of the calculated densities of odd-numbered oligothiophenes reported here are nevertheless significant even considering the above problem.
- 32 We also examined the set of lattice constants with duplicated value of c -axis (ca. 38 Å). The trial, however, did not fit well the observed diffraction: all the ($00l$) ($l = 2n + 1$) reflections are null.