

Structural and Conformational Studies of Quaterthiophenes Having Extra Bulky Terminal Groups

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An integrated set of experiments including crystallographic analysis and spectroscopy have been carried out to investigate structural and conformational features of tetramer oligothiophene compounds (quaterthiophenes). These quaterthiophenes are characterized by the presence of extra bulky terminal groups *N,N*-bis(trimethylsilyl)aminomethyl or (2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)alkyl, where the alkyl is methyl or ethyl. These bulky groups produce variation in molecular conformation and morphology. The X-ray analysis shows that two types of conformers are presently stable in the crystals: one is all-anti and the other is syn-anti-syn with respect to the molecular long axis. The molecular conformations have been further studied in solutions by spectroscopic methods, especially temperature-dependent ones. Of these, the UV-vis spectroscopy gives important information about the relative stability between the conformers. A clearly resolved isosbestic point means that two interconvertible conformers are present as the major species in the solutions. Numerical analysis of the spectra indicates that the free energy difference between these two is ~ 0.8 – 1.2 kcal/mol and that an absorption edge of the less stable conformer is significantly blue-shifted relative to the other. The former conformer is thought to be generated on account of the destruction of π -conjugation caused by distortion around the bonds connecting the thiophene rings. This associates the conformers with rotamers. The interconversion rate processes between these rotamers have been studied by the dynamic ¹H NMR spectroscopy. The line-width analysis of the coalesced spectral lines that are observed for the coupled protons implies that the free energy of activation for the interconversion is around 20 kcal/mol. These spectroscopic data are compared with the results of the quantum chemical calculations.

Introduction

Crystal structures and conformations of conjugated polymers and oligomers are currently being studied extensively. Among these materials, polythiophenes and oligothiophenes continue drawing particularly great attention. A good deal of crystallographic and spectroscopic information has been accumulated to interpret their structural and conformational features.

In a rigid lattice of the polythiophene, polymer chains assume the fully stretched S-anti conformation¹ and are packed in a well-known herringbone structure² where the S-anti planar macromolecules somewhat turn aside from the face-to-face arrangement; this structure is quite often observed for many organic crystals. Mean-

while, the polythiophenes appropriately substituted with various chemical groups such as alkyl^{3,4} show interesting structural characteristics on account of these substituents. In the alkyl-substituted polymers, for instance, the polythiophene backbone planes that have the S-anti conformation as well are forced to take the rigorous face-to-face polymer chain packing. Other interesting aspects of these polymers can be observed in solutions as chromisms.⁵ These chromisms result from the fact that a variety of conformations allowed in the solutions are coupled to the electronic states of the π -conjugated system. The conformational change accompanied by a color change is believed to be associated with the rotational defects (rotamers) introduced upon dissolution of the polymers, these defects breaking up the π -conjugation and causing segmentation or localization of the electronic wave functions.⁶

To study the variation in the crystal structures and molecular conformations more precisely, the oligoth-

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iophenes are particularly suited since their chemical structure can be tailored as desired and the crystals of high quality for the structure analysis are readily accessible. In particular, the oligothiophenes having long or bulky side/end groups on various positions of the backbone give an interesting variation in the crystal structures and molecular conformations. For instance, in crystals of α,ω -bis(trimethylsilyl)sexithiophene⁷ and related compounds of pentamer⁸ and hexamer^{8,9} various conformers (or rotamers) can be visualized as a consequence of distortion around the inter-ring σ -bonding.

Having these circumstances as a background, we have studied the structural and conformational characteristics of a specially selected set of oligothiophenes in both the crystals and solutions. These compounds are featured by extra bulky terminal groups¹⁰ and the following aspects ensue from their presence: (i) The bulky terminal groups introduce relatively large intermolecular steric hindrance between them. At the same time, the presence of these bulky groups results in loose packing of the oligothiophene backbones, which may lead to their conformational variation in the solid state. (ii) In the solutions, in turn, the bulky terminal groups are expected to influence the dynamics of the whole molecule because of, e.g., the large moment of inertia of these bulky groups.

The compounds investigated in the present studies are 5,5'''-bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl]-2,2':5',2'':5'',2'''-quaterthiophene (**1**), 5,5'''-bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)ethyl]-2,2':5',2'':5'',2'''-quaterthiophene (**2**), and 5,5'''-bis[*N,N*-bis(trimethylsilyl)aminomethyl]-2,2':5',2'':5'',2'''-quaterthiophene (**3**); see Figure 1 for the chemical structure. Although these compounds have been originally obtained as intermediates for aminoalkyl-terminated oligothiophenes,^{10,11} the intermediates turned out to be quite stable in the absence of acids. In such an environment the materials crystallize in needles or plates of high quality and can be even vacuum-processed into thin films without causing chemical degradation or alteration.¹² We present in this article the results obtained from a coordinated set of experiments. The results of the quantum chemical calculations are also presented.

Experimental Section

Synthesis of 5,5'''-Bis[*N,N*-bis(trimethylsilyl)aminomethyl]-2,2':5',2'':5'',2'''-quaterthiophene (3**).** Syntheses and crystal growths of **1** and **2** are described in the previous report.¹⁰ Compound **3** was synthesized as follows: Ethylmagnesium bromide ether solution (3 M, 78.7 mL, 0.236 mol) was added to a solution of 2-(aminomethyl)thiophene (12.4 g, 0.11 mol, Lancaster) in 80 mL of ether and the mixture was

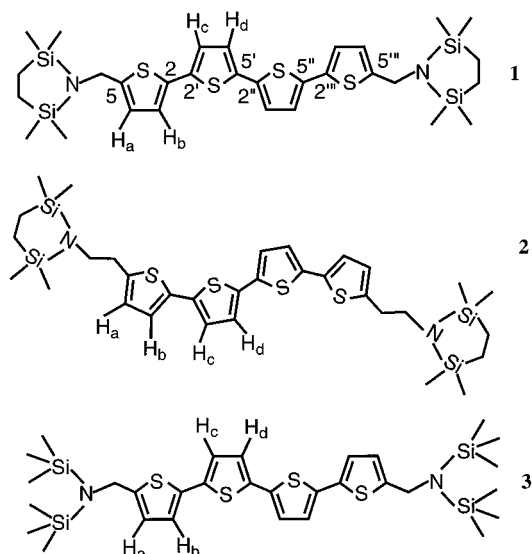


Figure 1. Chemical structure and conformation of **1**, **2**, and **3**. The backbone conformation is either all-anti (for **1** and **3**) or syn-anti-syn (for **2**). H_a , H_b , H_c , and H_d indicate the assignments of the protons in the 1H NMR spectra (see Figure 5 and the relevant text). The carbon numbering is supposed to start from the leftmost ring.

refluxed for 2 h. Chlorotrimethylsilane (25.7 g, 0.236 mol) in 50 mL of ether was then added, and the solution was refluxed further for 4 h. The resulting solution was washed, dried over K_2CO_3 , and evaporated to yield a pale yellow liquid. This liquid was distilled at 85 °C under reduced pressure 2–3 Torr, giving a viscous colorless liquid of 2-[*N,N*-bis(trimethylsilyl)aminomethyl]thiophene (**4**), yield 15.4 g, 55%. 1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.12 (dd, 1H, $^3J_{5,4} = 4.9$ Hz, $^4J_{5,3} = 1.2$ Hz, 5-H of thiophene); 7.00 (dd, 1H, $^3J_{4,5} = 4.9$ Hz, $^3J_{4,3} = 3.7$ Hz, 4-H of thiophene); 6.81 (dd, 1H, $^3J_{3,4} = 3.7$ Hz, $^4J_{3,5} = 1.2$ Hz, 3-H of thiophene); 4.22 (s, 2H, CH_2N); 0.11 (s, 18H, $SiCH_3$).

A solution of **4** (5.1 g, 20 mmol) in 80 mL of ether was cooled to 0 °C under dry nitrogen. *n*-BuLi/hexane (1.6 M, 13.75 mL, 22 mmol, Aldrich) was then added dropwise, causing the solution to turn dark purple. After 30 min, $MgBr_2 \cdot OEt_2$ (5.68 g, 22 mmol) was added and allowed to warm to room temperature. After a further 30 min, $Ni(dppp)Cl_2$ (0.16 g, 0.033 mmol) was fed, followed by the immediate addition of 5,5'-dibromo-2,2'-bithiophene (2.6 g, 8 mmol), which was prepared beforehand by mixing 2,2'-bithiophene (Aldrich) and *N*-bromosuccinimide (NBS) in methanol and subsequently recrystallizing the generated white precipitates from acetone.¹³ The solution was stirred overnight and refluxed for 4 h. The resulting deposits were filtered and recrystallized from hexane to give yellow thin blade-shaped crystals (**3**), yield 1.9 g, 36%. 1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.03 (d, 2H, $^3J = 3.7$ Hz, ring); 7.01 (d, 2H, $^3J = 3.7$ Hz, ring); 6.98 (d, 2H, $^3J = 3.7$ Hz, ring); 6.72 (d, 2H, $^3J = 3.7$ Hz, ring); 4.19 (s, 4H, CH_2N); 0.14 (s, 36H, $SiCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 1.85, 44.45, 123.21, 123.23, 123.56, 123.97, 134.67, 135.36, 136.84, 150.45. UV-vis in $CHCl_3$, λ_{max} 404 nm at room temperature. Anal. Calcd for $C_{30}H_{48}N_2S_4Si_4$: C, 53.20; H, 7.14; N, 4.14; S, 18.94. Found: C, 53.50; H, 7.09; N, 4.25; S, 18.61.

X-ray Crystallography. X-ray data of the single crystals **1–3** were collected using a Mac Science MXC18 four-circle diffractometer with Cu $K\alpha$ radiation at room temperature under ambient environment. Neither decay corrections nor absorption corrections were made. Data analysis was carried out with the CRYSTAN program. The structure was solved by the direct method on a MULTAN and refined by the full-matrix least-squares method using reflections whose intensities were more than 3 times greater than their standard

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Table 1. Crystallographic Data for 1, 2, and 3

compound	1	2	3
formula	C ₃₀ H ₄₄ N ₂ S ₄ Si ₄	C ₃₂ H ₄₈ N ₂ S ₄ Si ₄	C ₃₀ H ₄₈ N ₂ S ₄ Si ₄
formula weight	673.3	701.4	677.3
crystal color, habit	yellow, needle	yellow, plate	yellow, plate
crystal size (mm)	0.45 × 0.45 × 0.15	0.35 × 0.30 × 0.15	0.35 × 0.30 × 0.20
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>
<i>a</i> (Å)	16.609(4)	19.809(4)	17.459(3)
<i>b</i> (Å)	12.408(2)	6.158(1)	6.3377(8)
<i>c</i> (Å)	9.073(1)	15.749(2)	17.001(3)
β (deg)	91.88(2)	97.20(1)	94.62(1)
<i>V</i> (Å ³)	1868.7(6)	1906.0(5)	1875.0(5)
<i>Z</i>	2	2	2
<i>F</i> (000)	716	748	724
<i>D</i> _{calc} (g/cm ³)	1.20	1.22	1.20
λ (Å)	1.54178	1.54178	1.54178
μ (Cu Kα) (cm)	35.80	35.26	35.68
2θ range (deg)	3–130	3–130	3–130
index range <i>h, k, l</i>	0–19, 0–14, ±10	0–23, –7–0, ±18	±20, 0–7, 0–19
total reflns	3495	3731	3686
unique reflns	3107	3170	3127
reflns used in refinement	2878	2924	2887
no. of variables	248	263	254
<i>R</i> ^a	0.060	0.044	0.055
<i>R</i> _w ^b	0.093	0.046	0.063
GOF	1.27	2.47	1.95

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

deviations. All the non-hydrogen atoms were refined anisotropically.

Spectroscopic Measurements. UV–vis spectra were recorded in a 20 μM toluene solution of the oligothiophene at various temperatures covering –10 to 80 °C with a Ubest-50 (Japan Spectroscopic Co., Ltd.) equipped with a temperature controller using a Peltier effect. The toluene solutions were sealed in a quartz cuvette to ensure against loss of volatile solvent during the course of the measurements. The measurement temperatures may involve errors within ±1 °C.

¹H NMR spectra were measured at 500 MHz using a JEOL JNM-A500 spectrometer equipped with standard variable-temperature devices. The measurements were carried out either in deuteriochloroform at room temperature or in deuteriotoluene to cover a temperature range –30 to 110 °C. The measurement temperatures may involve errors within ±3 °C. ¹H COSY spectra were also collected with the same apparatus at room temperature. The sample concentrations were 15–40 mM, and the chemical shifts were referred to tetramethylsilane (TMS) for both the ¹H NMR and ¹H COSY experiments.

Quantum Chemical Calculations. Semiempirical calculations were performed using CACheMOPAC 94 software on a Macintosh Centris 650 equipped with a CXP 40/40 coprocessor. Preliminarily, we tried the PM3¹⁴ and AM1¹⁵ methods and compared them by optimizing the molecular geometry, starting from that determined crystallographically. The optimized geometry reached that includes the bond lengths and angles as well as the overall molecular shape is related to the starting geometry with the PM3 method better than with the AM1, and so we chose the PM3 for subsequent calculations.

Results

A. Crystallographic Data. *Crystal structures:* Crystallographic results of 1–3 are collected in Table 1. The atom numbering scheme is shown in Figure 2.

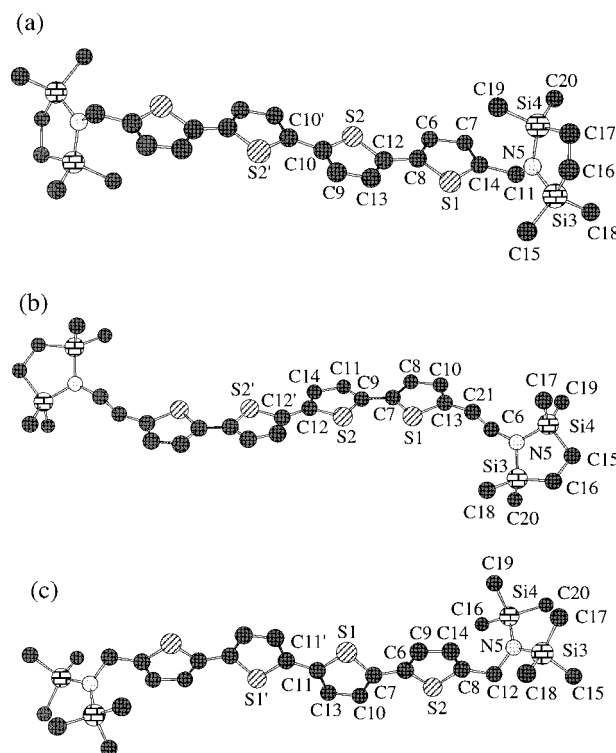


Figure 2. Molecular structure and atomic numbering for 1 (a), 2 (b), and 3 (c). C(10'), S(2'), etc., are given by the inversion of the corresponding C(10), S(2), etc. relative to the molecule center.

The crystals of all the compounds belong to the space group *P2*₁/*c*, and the molecules have the center of symmetry accordingly. For instance, in 1 the coordinates of C(10'), S(2'), etc., are given by the inversion of the corresponding C(10), S(2), etc., relative to the molecule center [i.e., the center of the C(10)–C(10') bond] which is positioned at the center of the crystal axis of the unit cell (see Figure 3). All the thiophene rings are nearly coplanar, and the methylene carbons directly bonded to the outer thiophene rings are posi-

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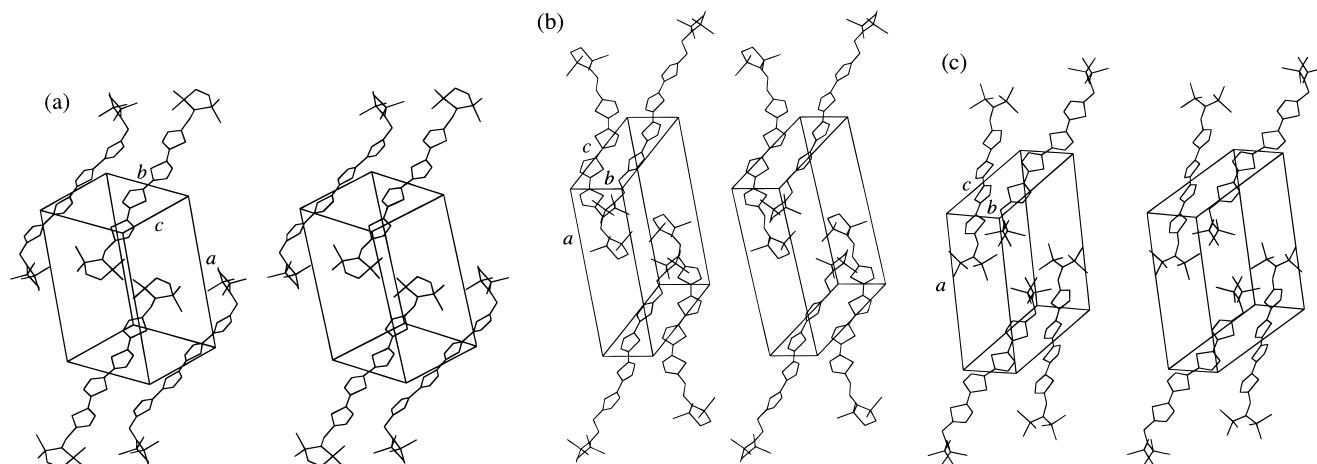


Figure 3. Stereoviews of the molecular packing for the crystals **1** (a), **2** (b), and **3** (c).

tioned very close to the coplanar backbone plane comprising the four thiophene rings.

Figure 3 shows stereoviews of crystals **1–3**. The overall crystallographic profile is characterized by a layered structure in which two-dimensionally spreading molecular “sheets” are stacked up along the *a* axis. The molecular long axis meets with the *a* axis at an angle of 62.4°, 53.2°, and 59.1° for **1**, **2**, and **3**, respectively. These crystallographic features accompanied by the $P2_1/c$ (or $P2_1/a$) space group are very often observed for crystals of both aromatic^{2b} and aliphatic¹⁶ hydrocarbons whose molecules have a well-defined molecular long axis.

The bulky terminal groups largely turn aside from the backbone plane. As regards **1** and **2**, the least-squares plane of the five-membered ring of azadisilacyclopentyl in the terminal group and that of the outer thiophene ring cross at an angle 100.3° and 121.8°, respectively. For **3** the plane consisting of the nitrogen and two silicon atoms of the terminal group meets at an angle 107.3° with the least-squares plane of the outer thiophene ring. Owing to the presence of these terminal groups, the molecules glide over one another. As a result, portions covering merely two thiophene rings overlap each other within a pair of adjacent molecules. This is similarly the case with a sexithiophene derivative having bulky triisopropylsilyl groups.⁷

In **1**, furthermore, the bulky terminal groups force the crystals to lack the herringbone structure and the overlapping molecules to be related by the translation.¹⁷ The dihedral angle between the two least-squares planes of the overlapping thiophene rings is 3.6° in this arrangement. Another specific feature of **1** is that within the terminal groups 2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl, a short intermolecular contact of 3.731(8) Å is observed between two methyl carbons C(18) and C(19). Notice that these two methyl carbons face almost right in front of each other. This contact is significantly smaller than two times van der Waals radius of a methyl group (~2 Å),¹⁸ meaning the presence of strong intermolecular interaction (or steric hindrance) between the terminal groups. The shortest atomic

contact between the molecules is 3.566(3) Å for S(2)⋯C-(7). This is pretty close to the sum of the van der Waals radius of each atom (~1.7 Å for carbon¹⁹ and ~1.8 Å for sulfur¹⁹). A bithiophene compound²⁰ with the same terminal groups as **1** shows a virtually identical molecular packing scheme.

Molecular structures: The most striking feature associated with the molecular structure is that two distinct nearly coplanar conformations can be noticed (Figures 1 and 2). One is all-anti (for **1** and **3**) and the other is syn-anti-syn (for **2**). For both conformations, the centrosymmetry in the crystals necessarily requires the two centermost thiophene rings to take the anti conformation relative to the molecular long axis (a line linking the methylene carbons bonded to the thiophene rings). Consequently, the coplanarity encompassing these two rings is rigorously achieved; the deviation of the individual atoms on these rings from the least-squares plane defined by those atoms is at most 0.007 Å for all the compounds. The outer ring is almost completely planar as well; the deviation of the atoms on the outer ring from its least-squares plane is also at most 0.007 Å. The two least-squares planes meet at an angle of 3.6, 5.0, and 12.1° for **1**, **2**, and **3**, respectively. From the symmetry requirement the said angle for **1** is exactly the same as the dihedral angle between the thiophene rings overlapping in the adjacent pair of molecules. Note that rather unusual S-syn forms are found as disorder or as crystallographically independent components in the compounds also having relatively large substituents.^{8,21} A “noncoplanar” syn conformer is also observed for a β -methyl-substituted quaterthiophene.²²

The selected bond lengths and angles for **1**, **2**, and **3** are collected in Tables 2, 3, and 4, respectively. The S–C bonds of **1**, **2**, and **3** exhibit closely related lengths in the ranges 1.723(3)–1.727(3), 1.721(3)–1.732(3), and 1.721(3)–1.735(3) Å, respectively, being contrasted with 1.717(7)–1.750(6) Å for 5,5′′-dimethyl-2,2′:5′,2′′:5′′,2′′′-

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1^a

S1-C14	1.725(3)	C8-C12	1.453(4)
S1-C8	1.727(3)	C9-C10	1.363(5)
S2-C10	1.723(3)	C9-C13	1.407(5)
S2-C12	1.726(3)	C11-C14	1.503(4)
C6-C8	1.360(5)	C12-C13	1.354(4)
C6-C7	1.425(5)	C10-C10'	1.453(6)
C7-C14	1.347(4)		
C14-S1-C8	92.4(1)	C13-C12-C8	129.9(3)
C10-S2-C12	92.4(1)	C13-C12-S2	110.5(2)
C8-C6-C7	113.3(3)	C8-C12-S2	119.6(2)
C14-C7-C6	113.1(3)	C12-C13-C9	113.4(3)
C6-C8-C12	127.8(3)	C7-C14-C11	127.4(3)
C6-C8-S1	110.2(2)	C7-C14-S1	111.0(2)
C12-C8-S1	122.0(2)	C11-C14-S1	121.6(2)
C10-C9-C13	113.5(3)	C9-C10-C10'	129.9(4)
C9-C10-S2	110.2(2)	S2-C10-C10'	119.9(3)

^a The data are only for the atoms included in the quaterthiophene backbone. This also applies to Tables 3 and 4.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

S1-C13	1.721(3)	C9-C11	1.362(4)
S1-C7	1.726(3)	C10-C13	1.350(5)
S2-C9	1.723(3)	C11-C14	1.408(5)
S2-C12	1.732(3)	C12-C14	1.358(4)
C7-C8	1.364(4)	C13-C21	1.505(5)
C7-C9	1.455(4)	C12-C12'	1.450(5)
C8-C10	1.435(5)		
C13-S1-C7	92.6(2)	C13-C10-C8	114.0(3)
C9-S2-C12	92.7(1)	C9-C11-C14	113.2(3)
C8-C7-C9	128.0(3)	C14-C12-S2	109.7(2)
C8-C7-S1	110.9(2)	C10-C13-C21	129.6(3)
C9-C7-S1	121.0(2)	C10-C13-S1	110.5(2)
C7-C8-C10	111.9(3)	C21-C13-S1	119.9(3)
C11-C9-C7	127.7(3)	C12-C14-C11	114.1(3)
C11-C9-S2	110.3(2)	C14-C12-C12'	129.7(3)
C7-C9-S2	122.0(2)	S2-C12-C12'	120.6(3)

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

S1-C11	1.725(3)	C8-C14	1.355(5)
S1-C7	1.735(3)	C8-C12	1.507(5)
S2-C8	1.721(3)	C9-C14	1.409(5)
S2-C6	1.732(3)	C10-C13	1.406(5)
C6-C9	1.361(5)	C11-C13	1.368(5)
C6-C7	1.442(4)	C11-C11'	1.451(6)
C7-C10	1.364(5)		
C11-S1-C7	92.5	C14-C8-S2	110.3(2)
C8-S2-C6	92.7(2)	C12-C8-S2	120.2(2)
C9-C6-C7	129.9(3)	C6-C9-C14	113.6(3)
C9-C6-S2	109.7(2)	C7-C10-C13	113.4(3)
C7-C6-S2	120.2(2)	C13-C11-S1	110.2(2)
C10-C7-C6	130.0(3)	C11-C13-C10	113.8(3)
C10-C7-S1	110.2(2)	C8-C14-C9	113.7(3)
C6-C7-S1	119.7(2)	C13-C11-C11'	129.3(4)
C14-C8-C12	129.5(3)	S1-C11-C11'	120.5(3)

quaterthiophene (DMQtT)^{23a} in which the bond lengths range considerably widely. Moreover, the bond angles C-S-C of **1**, **2**, and **3** also show related values 92.4(1), 92.6(2)–92.7(1), and 92.5(2)–92.7(2)°, respectively. These angles are also compared with the corresponding angles 91.4(3)–92.6(3)° for DMQtT.²³ These data verify that the ring deformation is smaller in the quaterthiophenes of the present studies than in DMQtT. Seeing that the ring deformation in DMQtT results from the tight packing of the molecules in the crystal lattice,²³ the

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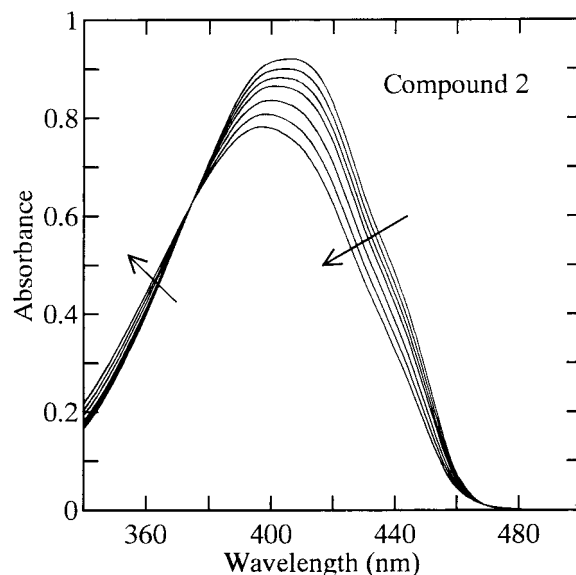


Figure 4. UV-vis spectra of **2** in toluene measured at -10, 0, 10, 20, 40, 60, and 80 °C. The direction of the arrows follows the increasing measuring temperatures.

small ring deformation in **1–3** is ascribable to the loose packing of the oligothiophene backbones. This packing scheme is likely to result from the incomplete overlap between the molecules and to allow various conformers to be stabilized according to a change in the crystallographic environment that is brought about by the subtle modification of the bulky terminal groups. This, at the same time, suggests that the energy level of those conformers is close (vide infra).

B. Spectroscopic Data in Solutions. *UV-Vis spectra:* A typical example of the temperature-dependent UV-vis spectra in toluene is shown for **2** in Figure 4. The spectral profiles of all the compounds are closely related to one another, reflecting the electronic structure of the quaterthiophene backbone. The absorption maxima of those spectra are located around 400 nm. Distinct isosbestic points are observed at 376, 374, and 376 nm for **1**, **2**, and **3**, respectively, within ± 1 nm accuracy. This demonstrates that two interconvertible conformers are present as the major species under thermodynamic equilibrium.

In this case we can readily determine on the basis of the data of Figure 4 the free energy difference (ΔG) between the two conformers using a standard process.^{24,25} We have carried out the numerical computation examining various trial combinations ϵ_A and ϵ_B (where ϵ_A and ϵ_B are molar absorption coefficients of the conformers A and B, respectively, with A more stable than B) at an appropriately fixed wavelength. For each combination of ϵ_A and ϵ_B a standard deviation (Δ) of ΔG can be defined as follows:

$$\Delta = \left\{ \sum_i [(\Delta G_i - \bar{\Delta G}) / \bar{\Delta G}]^2 \right\}^{1/2} \quad (1)$$

where $\bar{\Delta G}$ is an average of ΔG_i (the subscript i denotes the individual temperature measured). If minimum Δ

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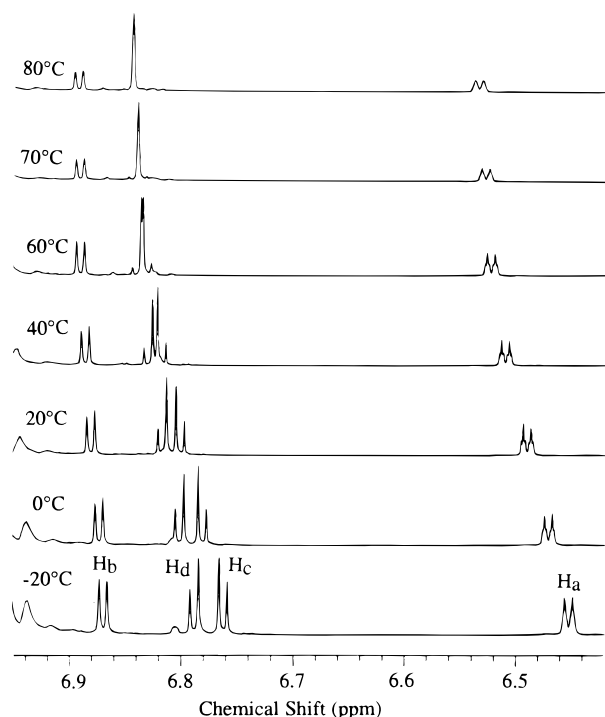


Figure 5. Temperature-dependent ^1H NMR spectra of the aromatic protons of **2** measured in deuteriotoluene. The assignments of these protons are indicated in Figure 1.

is reached after the trial calculations, the $\Delta\bar{G}$ determined correspondingly to that minimum most likely represents the free energy difference between the two conformers in the temperature range of the measurements. Thus, a reasonable value of ΔG for all the compounds turned out to range from 0.8 to 1.2 kcal/mol, for which the smallest deviations Δ within a few percent were reached.

During the course of the numerical computations, we have found out that at a wavelength longer than ~ 390 nm (corresponding to ~ 3.18 eV) $\epsilon_{\text{B}}/\epsilon_{\text{A}} \approx 0$ gives the most probable solution. This implies that the less stable conformer B has an absorption edge at ~ 3.18 eV, even though the absorption edge in the real spectra occurs at 2.58 eV (480 nm) owing to the more stable species A (Figure 4). The less stable species have an increasing contribution in the spectra with increasing temperatures, causing a blue-shift in the absorption maxima.

^1H NMR spectra: The temperature-dependent spectra of the aromatic protons in deuteriotoluene are represented for **2** in Figure 5. The assignment of the peaks has been done by COSY spectra and on the basis of the previous assignment for analogous compounds.²⁶ Figure 5 shows that the coupled quartet peaks due to H_{c} and H_{d} cause a downfield shift with increasing temperatures with the difference in the chemical shift ($\Delta\nu$) between these protons smaller. These peaks finally coalesce at 65 °C. Although the corresponding peaks of **3** also coalesce at 107 °C, those peaks of **1** do not coalesce within the experimental range of the temperatures (up to 110 °C).

Since the chemical shift is strongly affected by the vicinal chemical environment,^{27,28} the fact that $\partial(\Delta\nu)/$

∂T of H_{c} is larger than that of H_{d} implies that during the conformers interconversion the chemical environment in the vicinity of H_{c} changes larger than that for H_{d} . This may be the origin of the coalescence. Although the coalescence is reported on various organic compounds,²⁹ it is for the first time to the best of our knowledge that the coalescence has been clearly observed regarding the oligothiophene system. We remark in this respect that Blanchard and co-workers²⁷ did report the occurrence of the coalescence for an oligothiophene in their first report but afterward withdrew it as apparent.

For the coupled system the interconversion rate constant (k) can be expressed as²⁹

$$k \approx (\pi/\sqrt{2})(\Delta\nu_{\text{c}}^2 + 6J^2)^{1/2} \quad (2)$$

where $\Delta\nu_{\text{c}}$ is the chemical shift difference between the coupled protons at an instant of the coalescence and is approximated by the fwhm (full width at half-maximum) of the coalesced line; J is their coupling constant. The applicability of eq 2, however, is valid only if $\Delta\nu_{\text{c}}$ exceeds the coupling constant.^{29d} In cases where $\Delta\nu_{\text{c}}$ is well below the coupling constant, the complete line-shape analysis^{29d} shows that the rate constant is rather approximated by a simpler form:^{29a}

$$k \approx (\pi/\sqrt{2})\Delta\nu_{\text{c}} \quad (3)$$

this expression being usually used for the uncoupled protons system. Since $\Delta\nu_{\text{c}}$ of **2** and **3** are 1.33 and 2.52 Hz, respectively, and J is 3.66 Hz, we presume that the rate constant is between those evaluated from eqs 2 and 3 (see Figure 2 of ref 29d).

It is well-established that the free energy of activation for the conformers interconversion (ΔG^\ddagger) is expressed by³⁰

$$\Delta G^\ddagger = 2.303 \times 10^{-3} RT_{\text{c}} \log(k_{\text{Boltzmann}} T_{\text{c}} / hk) \quad (4)$$

where T_{c} is the coalescence temperature, $k_{\text{Boltzmann}}$ the Boltzmann constant, and h the Planck constant. We assume the transmission coefficient to be unity.^{30,31} Since in our case the rate constant for the process A to B (k_{A}) and that for B to A (k_{B}) will not be identical, the individual constants may be defined using the averaged constant k obtained either in eq 2 or in eq 3 as³² $k_{\text{A}} = 2P_{\text{B}}k$ and $k_{\text{B}} = 2P_{\text{A}}k$ where P_{A} and P_{B} are populations

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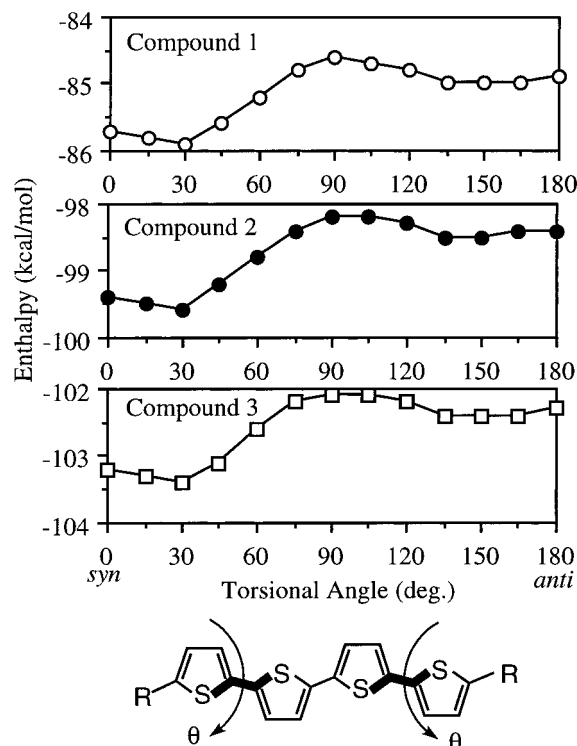


Figure 6. Enthalpy of the oligothiophenes as a function of the torsional angle θ around the 2,2' and 5'',2''' axes. The centermost rings are held at the anti conformation and the backbones retain the C_i symmetry after the inter-ring distortion.

of A and B, respectively. The constant k in eq 4 then must be replaced with either k_A or k_B . The populations can be determined on the basis of the electronic spectra (Figure 4).

Thus, we obtained as the free energy of activation ~ 17.3 – 19.0 (18.2 – 20.2) kcal/mol for the species B (A) of **2** and ~ 19.6 – 21.0 (20.5 – 22.1) kcal/mol for the species B (A) of **3**. For this estimation both the variation in the free energy difference (0.8–1.2 kcal/mol) and an error in the measuring temperatures (± 3 °C) were taken into account.

C. Quantum Chemical Calculations. There exist many rotamers according to torsional angles around the axes interconnecting the thiophene rings. The energy (E) of these rotamers can be expressed as follows as a function of these angles:

$$E = E(\theta_1, \theta_2, \theta_3) \quad (5)$$

where θ_1 , θ_2 , and θ_3 represent the torsional angles around the 2,2', 5',2'', and 5'',2''' axes, respectively (see Figure 1 where the carbon numbering is supposed to start from the leftmost ring). After optimizing the molecular geometry, we allowed only the inter-ring rotational freedom within the quaterthiophene backbone. The torsional angle is defined as a dihedral angle between the two planes determined by the thick lines drawn in Figure 6 such that this angle is zero at the syn position. We carried out the calculations, permitting various molecular symmetries and changing the number of axes that participate in the rotamers interconversion. The molecular symmetry was referred only to the quaterthiophene backbone.

Table 5. Enthalpy Data (kcal/mol) and the Point Group for Various Rotamers

compound	no. of axes	axis of distortion	point group ^a	ΔH^{\ddagger} ^b	ΔH^{\ddagger} (from syn) ^c	ΔH^{\ddagger} (from anti) ^d
1	1	5',2''	C_2	0.5	0.7	0.2
1	1	2,2'	C_1	0.4	0.6	0.2
2	1	5',2''	C_2	0.4	0.7	0.3
3	1	5',2''	C_2	0.5	0.7	0.2
1	2	2,2'; 5'',2'''	C_i	0.9	1.3	0.4
2	2	2,2'; 5'',2'''	C_i	1.1	1.4	0.3
3	2	2,2'; 5'',2'''	C_i	1.0	1.3	0.3
1	3	all bonds	C_2	1.3	1.9	0.6

^a The point group is referred only to the quaterthiophene backbone. ^b Enthalpy difference between the two minima. ^c Barrier enthalpy starting from the syn form. ^d Barrier enthalpy starting from the anti form.

In all the above cases, the energy (represented by enthalpy in the figure) of the rotamers shows a double minima as a function of the torsional angle θ , these minima being found at $\theta = 30^\circ$ (syn-periplanar or syn-gauche) and 150° (anti-periplanar or anti-gauche) with the former more stable than the latter by ~ 0.4 – 1.3 kcal/mol. The rotamers are destabilized most when each torsional angle is 90° . An example is shown in Figure 6, and the related results are summarized in Table 5. The relative stability between the rotamers and the barrier energies depend principally upon the number of the axes that participate in the inter-ring distortion regardless of the molecular symmetry. This is because the distortion around the individual bond gives rise to a similar level of energy instability³³ of ~ 0.4 – 0.5 kcal/mol per bond participating in the ring distortion. Therefore, if two (three) such bonds are involved in the distortion, the barrier energies and their difference are expected to be doubled (triplicated).³³

The energy difference between the two minima is expected to represent the free energy difference between the conformers; the barrier energies correspond to the free energy of activation for the conformers interconversion. Note for the latter case that the energy of 1.9 kcal/mol (Table 5) sets an upper limit to the barrier energy, because during the course of the interconversion all the three angles θ_1 , θ_2 , and θ_3 do not need to assume 90° all at once.

Discussion

On the basis of the structural and spectroscopic results collected in both the solids and solutions, we discuss their physicochemical implications referring to the results of the quantum chemical studies.

Although the vibronic structure reflecting the presence of the well-defined molecular symmetry^{23,25,34,35} is always inconspicuous in the solution spectra, the absorption edge observed at 2.58 eV for the more stable conformer is pretty close to that for the thin films (~ 2.5 eV)¹² where the molecules assume a planar conformation. This implies that this conformer in the solution

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is quasiplanar despite causing symmetry lowering. The occurrence of an absorption edge at a considerably short wavelength in the other conformer is due to the interring distortion that breaks the π -conjugation.^{5,6} In this context, the conformers we are dealing with are *rotamers*. We conclude from this that the more stable rotamer is more extended and that the less stable one is more twisted or coiled. Consequently, the conformers interconversion may be characterized as the quasiplanar-coiled one where the symmetry of both the rotamers is lowered to a greater or lesser extent. It should be emphasized that only two rotamers are present as the major species, as evidenced by the UV-vis spectra, despite the possibility of the presence of various conformers that correspond to a variety of combinations of θ_1 , θ_2 , and θ_3 giving the energy minima. Our conclusion is consistent with the results of the IR measurements by Hernández et al.³⁶ carried out in solution. They treat the conformers of the oligothiophenes in terms of a mean conjugation length (MCL), and they conclude that two conformers exist in the solution regarding a related material, DMQTT. One has MCL near 4 and the other has MCL between 2 and 3.

Although the quantum chemical calculations reproduce the free energy difference between the conformers pretty well, the barrier heights separating the conformers obtained from these calculations are admittedly too low to account for the free energy of activation for their interconversion. The calculated barrier height of at most 1.9 kcal/mol is contrasted with the free energy of activation estimated to be ~ 20 kcal/mol from the ^1H NMR. This made us assume the presence of the origins that the quantum chemical calculations ignored. This may be legitimated, e.g., by the inference by Ortí et al.³⁷ that the experimentally determined barrier height for bithiophene³⁸ is considerably larger than the theoretical estimates because of impediment from surrounding liquid-crystalline media.

One such extrinsic origin is the rotational diffusion of the molecules in solution that is based upon the interaction between those molecules as the solute and solvent molecules. This model deals with reorientation in liquid media of nonspherical molecules that are considered as rigid rotors, in terms of the rotational diffusion tensor.^{39,40} The tensor is associated with the moment of inertia. More precisely, after diagonalized the diffusion tensor components with respect to the principal axes are approximately inversely proportional to the three principal moments of inertia.³⁹ Although the free energy of activation for the rotational diffusion of the molecules was not expressed explicitly as a function of the tensor components, studies on cyclohexene by Pajak et al.⁴⁰ showed a trend to which a larger rotational diffusion tensor is associated with a smaller free energy of activation for the molecular reorientation. If this is generally the case, the rotational diffusion around the principal axis relevant to the smallest

Table 6. Moment of Inertia of the Oligothiophenes and Free Energy of Activation for the Interconversion of the Rotamers^a

compound	2,2' axis ($\times 10^{-46}$ kgm ²)	5',2'' axis ($\times 10^{-46}$ kgm ²)	free energy of activation (kcal/mol)
1	413	274	
2	357	1497	17.3–20.2
3	165	680	19.6–22.1
2,2'-bithiophene ^b	16		$\sim 5^b$

^a The moment of inertia is only for the left part relative to the axis (see text). ^b Reference 38.

principal moment of inertia will be first activated with the smallest free energy of activation.

Following this consideration, we infer that the above applies with the rotamers of the oligothiophenes. By intuition, the moment of inertia around the molecular long axis of the oligothiophenes is thought to be by far smaller than the others; think of the small separations of the individual atoms from this axis. Therefore, the rotation about this axis (more exactly, the 2,2' or 5',2'' axis) is expected to be most easily activated. Note, however, that the interconversion of the rotamers differs from the conventional rotational diffusion in that during this process the molecules can be regarded not as the rigid rotors but as a flexible system having inner rotational freedom around the chemical bonds. Here let us tentatively deal with the molecular motion assuming that the left portion relative to the 2,2' axis (or 5',2'' axis) causes the rotational diffusion, while the remaining right portion is permitted to remain stationary as a whole relative to a surrounding liquid medium. In this situation, we must consider both the energy given to activate the rotational diffusion and that for breaking the π -conjugation.

To make the treatment easier, we calculated the moments of inertia around the individual chemical bonds connecting the thiophene rings, limiting the freedom only to the rotation around either the 2,2' or 5',2'' axis and borrowing the relevant geometrical data from the crystals. The results are shown in Table 6 along with the free energies of activation for the rotamer interconversion determined from the coalescence data. The moments of inertia are only for the left portion relative to the axis. Again, Table 6 shows the trend to which the larger moment of inertia is apparently associated with the larger free energy of activation. Furthermore, the large difference between the moments of inertia around the 2,2' axis and the 5',2'' axis for **2** and **3** is likely to be responsible for the coalescence. This is because the rotational diffusion around the 5',2'' axis is hindered because of the large moment of inertia around this axis, leading to smaller change in the chemical environment in the vicinity of H_d compared to that for H_c.

Conclusion

The structures and molecular conformations of the oligothiophenes having the extra bulky terminal groups have been investigated by X-ray analysis and UV-vis and ^1H NMR spectroscopic methods. These bulky terminal groups make the structural and conformational features of the oligothiophenes stand out among the related compounds. The crystals are characterized by

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the molecular layered structure. In these crystals, the molecules of compounds **1** and **3** have the all-anti conformation, whereas those of the compound **2** have the syn-anti-syn form. The conformational variation in the crystals produced by the subtle modification in the terminal groups suggests that the relevant conformers have a close energy level.

We have studied the relative stability between them through the UV-vis spectroscopy carried out in the solutions. The results show that two interconvertible conformers are present under thermodynamic equilibrium with the free energy difference between the two ~ 0.8 – 1.2 kcal/mol. The detailed numerical analysis of the spectral data implies that of the two conformers one exhibits an absorption edge at ~ 480 nm (2.58 eV), while that of the other is located around 390 nm (3.18 eV). The latter conformer has an increasing contribution in the spectra with raised temperatures, causing the blue-shift in the absorption maximum. These spectroscopic results indicate that the two conformers are characterized as the rotamers. One is more extended, and the other is more distorted. This is consistent with the results of the IR measurements done in solution.³⁶

These rotamers can be best described quantitatively in terms of the torsional angles around the bonds connecting the thiophene rings. Within this framework, we carried out the quantum chemical calculations based on the PM3 method. These calculations show that the rotamers exhibit energy minima when they assume the syn-periplanar and anti-periplanar conformations, the former being more stable than the latter. The energy difference between the two was estimated to be about 0.4–0.5 kcal/mol per bond participating in the ring distortion. This reproduces appreciably well the level

of the free energy difference between the two conformers estimated from the numerical analysis of the UV-vis spectra in the solutions.

The dynamic methods of the ^1H NMR spectroscopy offer important information about the rate processes of the interconversion between the conformers. Analyzing widths of the lines at the instant of the coalescence that come from the coupled protons H_c and H_d , we estimated that the free energy of activation for the interconversion ranges from roughly 17 to 22 kcal/mol. This is significantly larger than the energies obtained by the quantum chemical calculations. The discrepancy is indicative of the presence of the origin that was disregarded in the quantum chemical calculations. We sought this origin from the rotational diffusion of the molecules in the solutions and found out that this model interprets the large free energy of activation pretty satisfactorily.

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Supporting Information Available: Tables of positional parameters, equivalent isotropic thermal parameters, bond lengths and angles, symmetry operations, and the relevant crystallographic information for **1**–**3** and temperature-dependent ^1H NMR spectra of aromatic protons in deuteriotoluene and temperature-dependent UV-vis spectra in toluene for compounds **1** and **3** (34 pages). See any current masthead page for ordering and Internet access instructions.

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