

Synthesis and Solid-State Structures of Dimethyl 2,2'-Bithiophenedicarboxylates

Martin Pomerantz,* Ananda S. Amarasekara, and H. V. Rasika Dias*

Department of Chemistry and Biochemistry, Box 19065, The University of Texas at Arlington,
Arlington, Texas 76019-0065

pomerantz@uta.edu

Received May 2, 2002

The syntheses of dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (**3**), dimethyl 2,2'-bithiophene-3,4'-dicarboxylate (**4**), and dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (**5**) are described. Single-crystal X-ray structural analysis of these compounds shows that the thiophene rings in **3** and **4** are nearly coplanar (dihedral angle close to 0°) and they adopt the anti sulfur conformation in the solid state. Further, the structure of **4** is in agreement with our previous suggestion that there is an electrostatic stabilization of the planar structure due to attraction of the 3-carbonyl oxygen to the sulfur of the distal ring. In **5**, however, the thiophene rings are nearly perpendicular (dihedral angle 75°), indicating considerable steric hindrance between the two large ester groups at the 3- and 3'-positions. Unlike compounds **3** and **4**, where the thiophene rings have the sulfur atoms anti, *the sulfur atoms in 5 are completely syn*. This is the first instance where a bithiophene has been shown to adopt a conformation where the sulfur atoms are completely syn. The solid-state conformations of **3**, **4**, and **5** are in agreement with ab initio theoretical calculations on these compounds; particularly, the planar conformations of **3** and **4** reflect the previously calculated low rotation barriers of these molecules.

Introduction

Polythiophenes and oligothiophenes have attracted much interest in recent years due to their useful physical properties such as electrical conductivity and electroluminescence.¹⁻⁴ Electrical conductivity of the polythiophene system is due to the conjugated π system of the thiophene rings, and a planar arrangement of the rings is extremely important to make a better conducting polymer. Further, the light-emitting properties (electroluminescence and fluorescence) also change depending upon the degree of planarity of the system. There are number of theoretical studies⁵⁻⁷ on the conformations of the rings in bi- and oligothiophenes. In addition, there are various synthetic approaches to make planar arrangements of the thiophene rings in the 2,5-linked thiophene backbone of the polythiophenes. A number of methods have been employed in attempting to prepare planar bi-, tri-, and oligothiophene ring systems. These include bridging of the thiophene rings with an additional ring⁸ and using Roncali's ideas for rigidification of the system designed

to remove free rotation between adjacent rings by using other fused ring systems.⁴ In addition, Tour^{9,10} has introduced alternating donor and acceptor dipolar units into the polymer backbone.

Since polythiophene itself is insoluble in common organic solvents, many studies were directed toward the development of a better conducting polymer, with reasonably good solubility properties, which is useful in the processing of the polymer. Long chain alkyl substituents are known to improve the solubility of the polymer,^{11,12} but the steric effect of the substituent directly attached to the thiophene ring tends to twist the thiophene backbone. Regioregular head-to-tail (H-T) substituted poly(3-alkylthiophenes) are known to have improved electrical conductivity when compared with the corresponding nonregioregular polymer.¹³⁻¹⁶ This has been attributed to the ability of the thiophene rings to become coplanar. Recently, regioregular poly(3-hexylthiophene) was reported to show gate-induced superconductivity at 2.35 K.¹⁷

(1) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Ed.; Marcel Dekker: New York, 1998.

(2) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(3) Granstrom, M. *Polym. Adv. Technol.* **1997**, *8*, 424.

(4) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(5) Aleman, C.; Julia, L. *J. Phys. Chem.* **1996**, *100*, 1524.

(6) Orti, E.; Viruela, P. M.; Sanchez-Marin, J.; Tomas, F. *J. Phys. Chem.* **1995**, *99*.

(7) Pomerantz, M.; Cheng, Y. *Tetrahedron Lett.* **1999**, *40*, 3317.

(8) Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1268.

(9) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

(10) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355.

(11) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1985**, *53*, 79.

(12) Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 169.

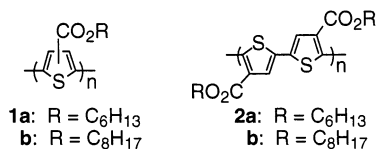
(13) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.

(14) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

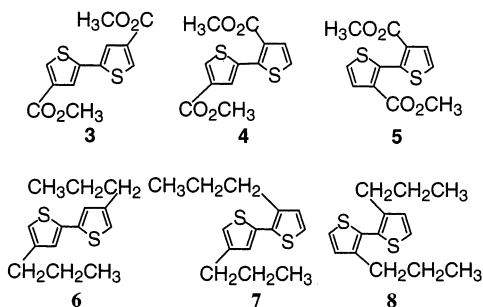
(15) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.

(16) Rieke, R. D.; Chen, T.-A. *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)* **1993**, *34* (No. 2), 426.

For a number of years we have been examining polythiophenes with ester functionalities directly attached to the thiophene rings, **1**, and have shown that they exhibit interesting electroluminescent properties.^{18–20} Our studies have involved long alkyl chain esters, since the alkyl chains afford greater solubility to the polymers. Examination of the UV–vis, fluorescence, and electrochromism properties of poly(hexyl thiophene-2,5-diyl-3-carboxylate) (**1a**) and poly(octyl thiophene-2,5-diyl-3-carboxylate) (**1b**), containing various amounts of head-to-head (H–H), head-to-tail (H–T), and tail-to-tail (T–T) linkages, depending on the method of preparation, and of the regioregular polymer poly[dihexyl (2,2'-bithiophene)-5,5'-diyl-4,4'-dicarboxylate] (**2a**) and poly[diocetyl (2,2'-bithiophene)-5,5'-diyl-4,4'-dicarboxylate] (**2b**) suggested that there was a large barrier to rotation around the thiophene–thiophene bond in the H–H linkages.²⁰



To study these systems further, to examine the stable conformations of the T–T, H–T, and H–H linkages, and to obtain the barriers to rotation about the various thiophene–thiophene linkages, we employed *ab initio* calculations [3-21G^(*)] on the corresponding bithiophene methyl esters, namely dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (**3**), dimethyl 2,2'-bithiophene-3,4'-dicarboxylate (**4**), and dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (**5**).⁷ In addition, for comparison, 4,4'-dipropyl-2,2'-bithiophene (**6**), 3,4'-dipropyl-2,2'-bithiophene (**7**), and 3,3'-dipropyl-2,2'-bithiophene (**8**) were similarly examined.⁷ Table 1 shows the calculated dihedral angle around the thiophene–thiophene bond for the most stable conformation and the rotational barrier, taken as the energy difference between the stable conformation and the energy of the molecules where the C–C–S dihedral angles were set at 0°. In all cases the geometries were optimized. There is one correction to the data previously reported and that is that the most stable conformation of the head-to-head bithiophene **5** has a C–C–S dihedral angle of 121.7° and a S–C–S



booxylate (**4**), and dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (**5**).⁷ In addition, for comparison, 4,4'-dipropyl-2,2'-bithiophene (**6**), 3,4'-dipropyl-2,2'-bithiophene (**7**), and 3,3'-dipropyl-2,2'-bithiophene (**8**) were similarly examined.⁷ Table 1 shows the calculated dihedral angle around the thiophene–thiophene bond for the most stable conformation and the rotational barrier, taken as the energy difference between the stable conformation and the energy of the molecules where the C–C–S dihedral angles were set at 0°. In all cases the geometries were optimized. There is one correction to the data previously reported and that is that the most stable conformation of the head-to-head bithiophene **5** has a C–C–S dihedral angle of 121.7° and a S–C–S

TABLE 1. Calculated [3-21G^(*)] Thiophene–Thiophene Dihedral Angles and Rotation Barriers for **3–8**^a

bithiophene	dihedral angle (deg)	rotation barrier [kcal/mol (kJ/mol)]
3	35.1	0.37 (1.5)
4	21.7 and 17.4	0.084 (0.35)
5	121.7	8.94 (37.4)
6	32.6	0.34 (1.4)
7	58.7 and 62.1	2.27 (9.5)
8	86.6	7.84 (33)

^a Reference 7.

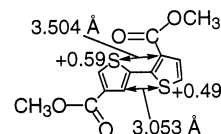
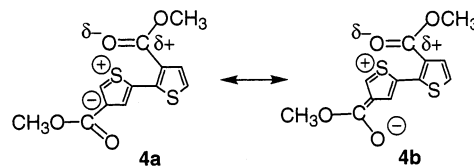


FIGURE 1. Carbon–sulfur distances and Mulliken charges on sulfur in **4**.

dihedral angle of 56.8°. Thus, in this molecule, the sulfur atoms are *syn* in the stable conformation. This will be discussed below. The difference in energy between the stable conformation with anti and *syn* sulfur atoms is only 0.40 kcal/mol (1.7 kJ/mol). This minimum was missed previously, and in the other systems the anti sulfur conformations are the global minima.

As was pointed out, the T–T systems, **3** and **6**, as well as the H–H systems, **5** and **8**, are similar and are what would be expected. The H–T propyl derivative **7**, is, as expected, right between **6** and **8**, but the H–T ester derivative, **4**, has both an abnormally low dihedral angle and a negligible rotation barrier.⁷ (Compounds **4** and **7** show two different dihedral angles each, since the two rings are not absolutely planar and the systems are rather asymmetric.) This was explained by suggesting that there is Coulombic stabilization of the positive charge on the sulfur atom by the partial negative charge on the carbonyl oxygen on the other ring. This causes the system to flatten and bend, resulting in a lower dihedral angle together with a lower rotation barrier.⁷ This is illustrated by the resonance forms such as **4a** and **4b**. This flattening in order to get the carbonyl oxygen



as close as possible to the sulfur atom causes the two rings to splay, which is shown by the approximately 0.5 Å difference in calculated distance between sulfur-1' and carbon-3 and sulfur-1 and carbon-3', as shown in Figure 1. Also in Figure 1 are the two different Mulliken charge densities, which also points up the Coulombic stabilization of additional positive charge on sulfur-1', as shown in resonance forms such as **4a** and **4b**.

We now report on the synthesis of the three bithiophene ester regioisomers **3–5** and on their X-ray crystal structures. We also compare the results in the solid state with the calculated structural parameters.

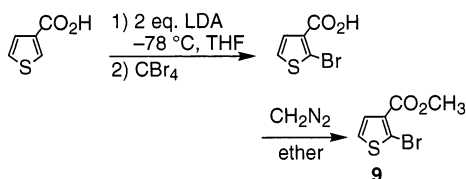
(17) Schön, J. H.; Dobabalapur, A.; Bao, Z.; Kloc, C.; Schenaker, O.; Batlogg, B. *Nature (London)* **2001**, *410*, 189.

(18) Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L. *Synth. Met.* **1997**, *85*, 1235.

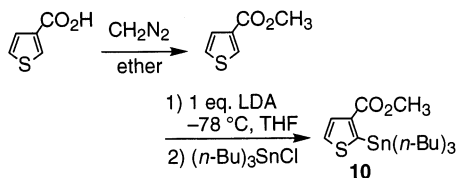
(19) Pomerantz, M.; Chang, Y.; Kasim, R. K.; Elsenbaumer, R. L. *Synth. Met.* **1999**, *101*, 162.

(20) Pomerantz, M.; Chang, Y.; Kasim, R. K.; Elsenbaumer, R. L. *J. Mater. Chem.* **1999**, 2155.

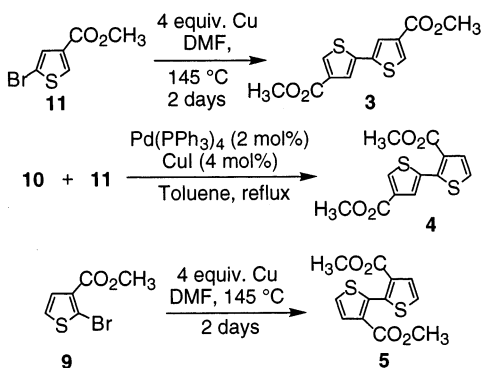
SCHEME 1



SCHEME 2



SCHEME 3



Results and Discussion

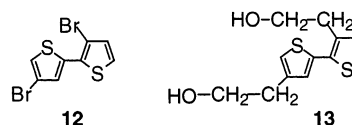
Scheme 1 shows the preparation of methyl 2-bromothiophene-3-carboxylate (**9**). Treatment of thiophene-3-carboxylic acid with 2 equiv of LDA at $-78\text{ }^{\circ}\text{C}$ followed by reaction of the dianion intermediate²¹ with CBr_4 gave 2-bromothiophene-3-carboxylic acid. Esterification with diazomethane afforded methyl 2-bromothiophene-3-carboxylate (**9**). Scheme 2 shows the preparation of methyl 2-(tri-*n*-butylstannyl)thiophene-3-carboxylate (**10**). Esterification of thiophene-3-carboxylic acid followed by treatment with 1 equiv of LDA and then with tri-*n*-butylchlorostannane gave methyl 2-(tributylstannyl)thiophene-3-carboxylate (**10**). Methyl 2-bromothiophene-4-carboxylate (**11**) was prepared as reported previously.^{20,22} The symmetrical bithiophenes **3** and **5** were prepared by Ullmann coupling^{20,23,24} ($\text{Cu}/\text{DMF}/145\text{ }^{\circ}\text{C}$) of the bromo esters **9** and **11**, while the unsymmetrical bithiophene **4** was synthesized by Stille coupling^{25,26} [$\text{Pd}(\text{PPh}_3)_4/\text{CuI}/\text{toluene}/\text{reflux}$] of **10** with **11**, as shown in Scheme 3.

T–T bithiophene **3** shows two low-field signals in the ^1H NMR spectrum at δ 7.58 and 8.00, with $J = 1.4\text{ Hz}$, which is characteristic of a 2,4-disubstituted thiophene.²⁷

H–H bithiophene **5** shows two signals at δ 7.34 and 7.52 with a coupling constant of 5.4 Hz, and this is characteristic of a 2,3-disubstituted thiophene.²⁷ The H–T bithiophene **4** shows four signals in the aromatic region, two doublets at δ 7.23 and 7.44 with $J = 5.5\text{ Hz}$, and two other doublets at δ 7.76 and 8.15 with $J = 0.9\text{ Hz}$, consistent with the structure.²⁷

The ORTEP drawings of the single-crystal X-ray structures of **3**, **4**, and **5** along with the side views of each are shown in Figures 2, 3, and 4, and structural parameters are given in Tables 2, 3, and 4. Dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (**3**), the T–T isomer, is unexceptional, showing essentially coplanar thiophene rings and the anti conformation of the sulfur atoms. The S–C(2)–C(2A)–C(3A) dihedral angle is 0.4° . The C2–C2A bond distance is 1.446 Å, which is very close to the 3-21G^(*) calculated value of 1.457 Å. The calculated dihedral angle of 35° is considerably different from the observed value, because the low rotation barrier allows the rings to become coplanar, due to packing forces in the solid state. This is in agreement with other bithiophenes, which are substituted at the 4- and 4'-positions.²⁸ The distance between the sulfur of one ring (S0A) and the carbon (C3) of the other ring is 3.211 Å, compared with the calculated value for the planar molecule of 3.221 Å (and 3.304 Å for the twisted conformation).

Dimethyl 2,2'-bithiophene-3,4'-dicarboxylate (**4**), the H–T isomer, is also observed to be very nearly flat with the sulfur atoms anti (Figure 3). The S2–C2'–C2–C3 and S1–C2–C2'–C3' dihedral angles of 2.7° and 3.8° are considerably less than the calculated values of 21.7° and 17.4° , respectively. Again, with a low calculated rotational barrier the bithiophene portion of the molecule is expected to be nearly planar. The S–C–C–S dihedral angle of 175.8° compares quite favorably with that for 3,4'-dibromo-2,2'-bithiophene (**12**), 175.0° .²⁵ The C3–S2



distance is 3.468 Å, while the S1–C3' distance is 3.025 Å compared to the calculated values of 3.494 and 3.027 Å for the planar conformation of **4**. The large difference in these two distances dramatically points up how the bithiophene distorts by having the two thiophene rings splay outward in order to accommodate the carbonyl oxygen atom near the sulfur on the other ring so that the maximum electrostatic stabilization can be achieved.⁷ The distance between the nonbonded atoms S2 and O1 of 2.668 Å, compared with the calculated distance in the flat conformation of 2.662 Å, is clearly extremely short, shorter than the sum of the van der Waals radii, 3.32 Å,²⁹ again attesting to the strong attraction between the sulfur and the carbonyl oxygen.⁷ The C2–C2' bond is

(21) Knight, D. W.; Nott, A. P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 791.

(22) Satonaka, H. *Bull. Chem. Soc. Jpn.* **1983**, 56, 3337.

(23) Fanta, P. E. *Chem. Rev.* **1964**, 64, 613.

(24) Fanta, P. E. *Synthesis* **1974**, 9.

(25) Antolini, L.; Goldoni, F.; Iarossi, D.; Mucci, A.; Schenetti, L. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1957.

(26) Akoudad, S.; Roncali, J. *Chem. Commun.* **1998**, 2081.

(27) Gronowitz, S.; Hörnfeldt, A.-B. In *Thiophene and Its Derivatives*; Gronowitz, S., Ed.; Wiley: New York, 1991; Vol. 44, Part 4, Chapter 1.

(28) Lukevics, E.; Barbarella, G.; Arsenyan, P.; Belyakov, S.; Pudove, O. *Chem. Heterocycl. Compd. (Engl. Transl.)* **2000**, 36, 630.

(29) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry-Part A: Structure and Mechanism*, 4th ed.; Kluwer Academic/Plenum Publishers: New York, 2000; p 126.

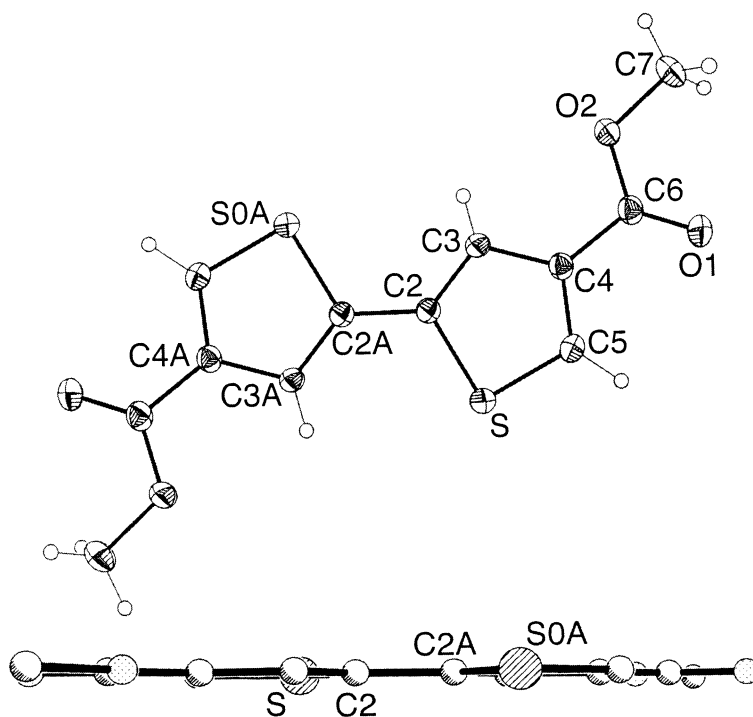


FIGURE 2. ORTEP drawing and side view of 3.

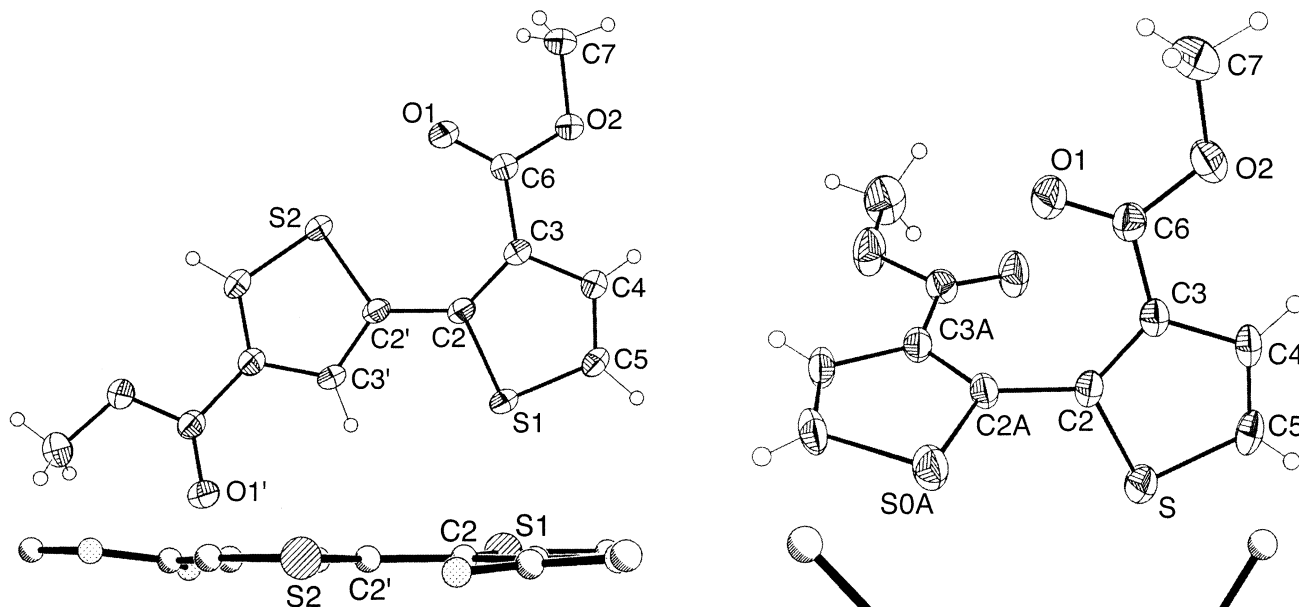


FIGURE 3. ORTEP drawing and side view of 4.

1.467 Å, which is exactly the same as the calculated value for the flat conformation.

Dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (5), the H-H isomer, also proved to be extremely interesting and novel. The hindrance of the bulky ester groups at the 3- and 3'-positions causes the bithiophene to twist as expected, but what was not expected was that the sulfur atoms are syn in this molecule (Figure 4). The S0A-C2A-C2-S dihedral angle is 74.8°, while the S0A-C2A-C2-C3 dihedral angle is 104.0°. The 3-21G^(*) calculated values are 56.8° and 121.7°, respectively.

The difference between the observed and calculated values is not known but probably has to do with the

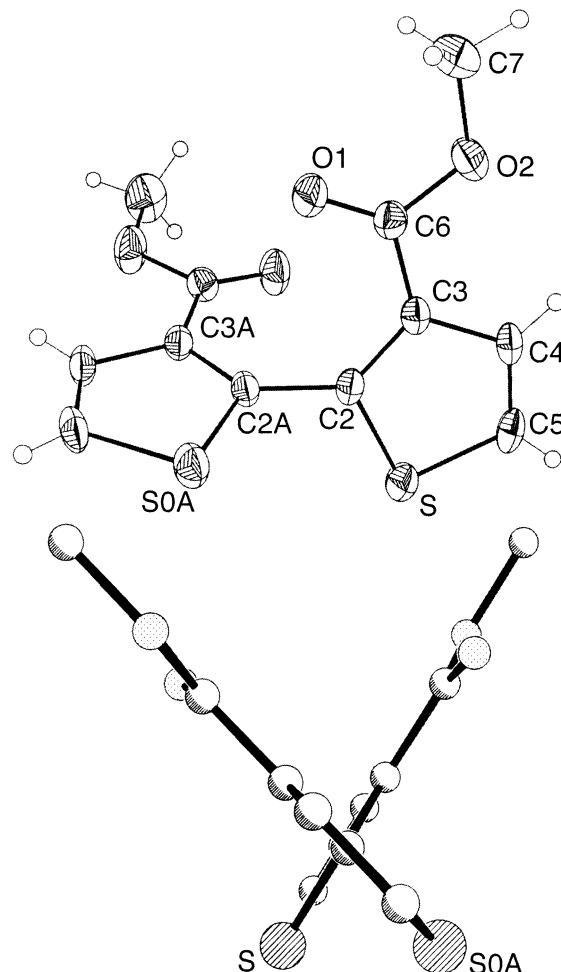


FIGURE 4. ORTEP drawing and side view of 5.

TABLE 2. Some X-ray Structural Parameters for 3

Bond Lengths (Å)			
S–C(5)	1.693(2)	C(2)–C(3)	1.353(3)
S–C(2)	1.730(2)	C(2)–C(2A)	1.446(4)
O(1)–C(6)	1.194(3)	C(3)–C(4)	1.411(3)
O(2)–C(6)	1.333(3)	C(4)–C(5)	1.352(3)
O(2)–C(7)	1.444(3)	C(4)–C(6)	1.479(3)
Bond Angles (deg)			
C(5)–S–C(2)	92.03(11)	C(5)–C(4)–C(6)	120.95(19)
C(6)–O(2)–C(7)	116.07(19)	C(3)–C(4)–C(6)	126.89(19)
C(3)–C(2)–C(2A)	130.3(2)	C(4)–C(5)–S	112.13(17)
C(3)–C(2)–S	110.08(16)	O(1)–C(6)–O(2)	123.9(2)
C(2A)–C(2)–S	119.62(19)	O(1)–C(6)–C(4)	124.3(2)
C(2)–C(3)–C(4)	113.60(19)	O(2)–C(6)–C(4)	111.78(18)
Dihedral Angles (deg)			
C(5)–S–C(2)–C(2A)	–179.9(2)	C(2)–S–C(5)–C(4)	0.08(19)
C(2A)–C(2)–C(3)–C(4)	179.9(3)	C(7)–O(2)–C(6)–O(1)	–1.4(4)
S–C(2)–C(3)–C(4)	0.3(2)	C(7)–O(2)–C(6)–C(4)	178.7(2)
C(2)–C(3)–C(4)–C(5)	–0.2(3)	C(5)–C(4)–C(6)–O(1)	–0.5(4)
C(2)–C(3)–C(4)–C(6)	179.4(2)	C(3)–C(4)–C(6)–O(1)	179.8(2)
C(3)–C(4)–C(5)–S	0.1(2)	C(5)–C(4)–C(6)–O(2)	179.4(2)
C(6)–C(4)–C(5)–S	–179.64(17)	C(3)–C(4)–C(6)–O(2)	–0.3(3)

TABLE 3. Some X-ray Structural Parameters for 4

Bond Lengths (Å)			
S(1)–C(5)	1.700(2)	C(2)–C(3)	1.385(3)
S(1)–C(2)	1.720(2)	C(2)–C(2')	1.467(3)
S(2)–C(5')	1.690(3)	C(2')–C(3')	1.363(3)
S(2)–C(2')	1.727(2)	C(3)–C(4)	1.425(3)
O(1')–C(6')	1.200(3)	C(3)–C(6)	1.464(3)
O(1)–C(6)	1.191(3)	C(3')–C(4')	1.410(3)
O(2')–C(6')	1.331(3)	C(4')–C(5')	1.344(3)
O(2)–C(7)	1.440(3)	C(4)–C(6')	1.470(3)
O(2)–C(6)	1.322(3)	C(4)–C(5)	1.328(3)
O(2)–C(7)	1.448(3)		
Bond Angles (deg)			
C(5)–S(1)–C(2)	93.04(11)	C(2')–C(3')–C(4')	114.0(2)
C(5')–S(2)–C(2')	91.71(11)	C(5')–C(4')–C(3')	111.3(2)
C(6')–O(2')–C(7)	115.9(2)	C(5')–C(4')–C(6')	125.2(2)
C(6)–O(2)–C(7)	115.6(2)	C(3')–C(4')–C(6')	123.5(2)
C(3)–C(2)–C(2')	134.4(2)	C(5)–C(4)–C(3)	114.0(2)
C(3)–C(2)–S(1)	109.64(15)	C(4')–C(5')–S(2)	113.28(18)
C(2')–C(2)–S(1)	115.96(15)	C(4)–C(5)–S(1)	111.46(18)
C(3')–C(2')–C(2)	124.6(2)	O(1')–C(6')–O(2')	123.7(2)
C(3')–C(2')–S(2)	109.71(16)	O(1')–C(6')–C(4')	124.8(2)
C(2)–C(2')–S(2)	125.67(16)	O(2')–C(6')–C(4')	111.6(2)
C(2)–C(3)–C(4)	111.8(2)	O(1)–C(6)–O(2)	121.9(2)
C(2)–C(3)–C(6)	126.29(19)	O(1)–C(6)–C(3)	126.4(2)
C(4)–C(3)–C(6)	121.88(19)	O(2)–C(6)–C(3)	111.70(19)
Dihedral Angles (deg)			
C(5)–S(1)–C(2)–C(3)	0.52(16)	C(3')–C(4')–C(5')–S(2)	–0.5(3)
C(5)–S(1)–C(2)–C(2')	179.41(16)	C(6')–C(4')–C(5')–S(2)	179.17(16)
C(3)–C(2)–C(2')–C(3')	–177.7(3)	C(2')–S(2)–C(5')–C(4')	0.61(19)
S(1)–C(2)–C(2')–C(3')	3.8(2)	C(3)–C(4)–C(5)–S(1)	0.1(3)
C(3)–C(2)–C(2')–S(2)	2.7(3)	C(2)–S(1)–C(5)–C(4)	–0.39(19)
S(1)–C(2)–C(2')–S(2)	–175.80(11)	C(7)–O(2)–C(6')–O(1')	–0.8(3)
C(5')–S(2)–C(2')–C(3')	–0.51(17)	C(7)–O(2)–C(6')–C(4')	179.1(2)
C(5')–S(2)–C(2')–C(2)	179.11(18)	C(5')–C(4')–C(6')–O(1')	–173.4(2)
C(2)–C(2)–C(3)–C(4)	–179.1(2)	C(3')–C(4')–C(6')–O(1')	6.3(3)
S(1)–C(2)–C(3)–C(4)	–0.5(2)	C(5')–C(4')–C(6')–O(2')	6.7(3)
C(2')–C(2)–C(3)–C(6)	0.2(4)	C(3')–C(4')–C(6')–O(2')	–173.65(18)
S(1)–C(2)–C(3)–C(6)	178.80(17)	C(7)–O(2)–C(6)–O(1)	–3.3(4)
C(2)–C(2')–C(3)–C(4')	–179.32(18)	C(7)–O(2)–C(6)–C(3)	176.7(2)
S(2)–C(2')–C(3')–C(4')	0.3(2)	C(2)–C(3)–C(6)–O(1)	4.6(4)
C(2')–C(3')–C(4')–C(5')	0.1(3)	C(4)–C(3)–C(6)–O(1)	–176.1(2)
C(2)–C(3)–C(4)–C(5)	–179.57(18)	C(2)–C(3)–C(6)–O(2)	–175.43(19)
C(2)–C(3)–C(4)–C(5)	0.3(3)	C(4)C(3)–C(6)–O(2)	3.8(3)
C(6)–C(3)–C(4)–C(5)	–179.1(2)		

intermolecular forces between adjacent molecules. That the molecule is severely twisted is unexceptional, but that the sulfur atoms are syn makes this the only bithiophene known where the sulfur atoms are completely syn.²⁸ Thus, for example, 3,3'-dimethoxy-2,2'-bithiophene has its sul-

TABLE 4. Some X-ray Structural Parameters for 5

Bond Lengths (Å)			
S–C(5)	1.706(3)	C(2)–C(3)	1.368(4)
S–C(2)	1.710(3)	C(2)–C(2A)	1.482(5)
O(1)–C(6)	1.197(3)	C(3)–C(4)	1.431(4)
O(2)–C(6)	1.333(4)	C(3)–C(6)	1.466(5)
O(2)–C(7)	1.433(5)		
Bond Angles (deg)			
C(5)–S–C(2)	92.28(15)	C(4)–C(3)–C(6)	125.1(3)
C(6)–O(2)–C(7)	116.7(3)	C(5)–C(4)–C(3)	113.4(3)
C(3)–C(2)–C(2A)	129.6(2)	C(4)–C(5)–S	111.4(2)
C(3)–C(2)–S	111.60(19)	O(1)–C(6)–O(2)	123.1(4)
C(2A)–C(2)–S	118.82(16)	O(1)–C(6)–C(3)	125.7(3)
C(2)–C(3)–C(4)	111.3(3)	O(2)–C(6)–C(3)	111.2(2)
C(2)–C(3)–C(6)	123.6(2)		
Dihedral Angles (deg)			
C(5)–S–C(2)–C(3)	–0.5(2)	C(3)–C(4)–C(5)–S	–0.6(4)
C(5)–S–C(2)–C(2A)	–179.5(2)	C(2)–S–C(5)–C(4)	0.6(3)
C(2A)–C(2)–C(3)–C(4)	179.2(3)	C(7)–O(2)–C(6)–O(1)	–0.8(5)
S–C(2)–C(3)–C(4)	0.2(3)	C(7)–O(2)–C(6)–C(3)	–179.7(3)
C(2A)–C(2)–C(3)–C(6)	–0.2(5)	C(2)–C(3)–C(6)–O(1)	4.5(5)
S–C(2)–C(3)–C(6)	–179.1(2)	C(4)–C(3)–C(6)–O(1)	–174.7(3)
C(2)–C(3)–C(4)–C(5)	0.2(4)	C(2)–C(3)–C(6)–O(2)	–176.6(3)
C(6)–C(3)–C(4)–C(5)	179.6(3)	C(4)–C(3)–C(6)–O(2)	4.2(5)

fur atoms anti and also happens to have the two thiophene rings coplanar. Furthermore, 3,3'-bis(2-hydroxyethyl)-2,2'-bithiophene (**13**) also exists in a conformation with the sulfur atoms anti, and it is stated that this bithiophene has a S–C–C–S dihedral angle of 110.8°, and the inter-ring twist angle of 67.5° is the largest ever measured for adjacent rings of α -conjugated oligothiophenes.³⁰ It should be pointed out that our measured 74.8° dihedral angle for **5** is larger than that for **13**. There are a few reports of mixtures of anti- and syn-sulfur conformations, deduced as the result of observed disorder in some bithiophene and oligothiophene X-ray crystal structures,^{28,31–34} but none where the sulfur atoms are completely syn. It should also be pointed out that the C2–C2A distance is 1.482 Å (compared with 1.467 Å calculated), and this is somewhat longer than the comparable bond in **4** (1.467 Å) and much longer than that in **3** (1.446 Å). This sequence is due, no doubt, to the increase in steric effects along the series **3**–**5**.

Table 5 shows the UV spectra of compounds **3**–**5** in THF solution. Compound **4** shows longer wavelength absorption than **3**, indicating more conjugation, as shown by the resonance forms presented in Figure 5. In principle, **5** should show even greater conjugation,³⁵ except that the system is the most severely twisted, so there is an attenuation of this conjugation, resulting in the long wavelength maximum being between those of **3** and **4**.

Conclusion

Both dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (**3**) and dimethyl 2,2'-bithiophene-3,4'-dicarboxylate (**4**) have been shown to adopt planar structures in the solid state,

(30) Barbarella, G.; Zambianchi, M.; Bongini, A.; Antolini, L. *J. Org. Chem.* **1996**, *61*, 4708.

(31) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1597.

(32) Armes, S. P.; Chaloner, P. A.; Hitchcock, P. B.; Simmons, M. R. *Acta Crystallogr., Sect. C* **1994**, *50*, 1945.

(33) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *Acta Crystallogr., Sect. C* **1994**, *50*, 1941.

(34) Novak, I.; Ng, S. C.; Mok, K. F.; Mok, C. Y.; Huang, H. H. *J. Chem. Res., Synop.* **1992**, 350.

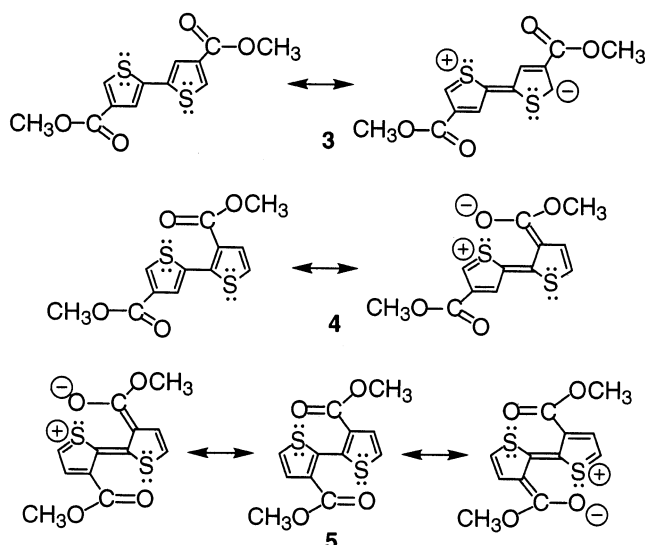


FIGURE 5. Some resonance forms for compounds 3–5.

TABLE 5. UV Spectra of Compounds 3–5 (THF solutions)

compd	λ_{\max} (nm) (ϵ)	
3	233 (25 000)	304 (7 600)
4	248 (22 000)	313 (13 000)
5	254 (15 000)	307 (7 000)

and the structure of 4 is in agreement with our previous suggestion, based on calculations, that there is an electrostatic attraction between the 3'-carbonyl oxygen (partial negative charge) and the sulfur of the distal ring (partial positive charge), resulting in a stabilization of the planar structure. In dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (5) the thiophene rings are severely twisted (S–C–C–S dihedral angle 74.8°) and the stable conformation is with the sulfur atoms syn. This is the first time a simple bithiophene (or oligothiophene) has been demonstrated to completely adopt the syn conformation.

Experimental Section

General. Melting points are uncorrected. NMR spectra were recorded using CDCl₃ solutions at 500.16 MHz with TMS ($\delta = 0.00$) as the internal reference for ¹H and at 125.78 MHz with CDCl₃ ($\delta = 77.00$) as the reference for ¹³C. FT-infrared spectra were recorded using KBr pellets or as a thin film between NaCl plates, and UV–vis spectra were taken using THF solutions. Elemental analyses were done by either Quantitative Technologies Inc., White House, NJ or using a Perkin-Elmer 2400 CHN analyzer at the University of Texas at Arlington.

2-Bromothiophene-3-carboxylic Acid. To a solution of diisopropylamine (3.03 g, 30 mmol) in 40 mL of dry tetrahydrofuran at –78 °C was added *n*-butyllithium (19.6 mL of a 1.43 M solution in hexane, 30 mmol) under an argon atmosphere. After stirring for 25 min, a solution of thiophene-3-carboxylic acid (1.92 g, 15 mmol) in 10 mL of dry tetrahydrofuran was added slowly during a 10 min period, the mixture was allowed to stand at –78 °C for an additional 20 min and it was then treated with a solution of CBr₄ (4.98 g, 15 mmol) in 10 mL of dry tetrahydrofuran. The cooling bath was removed and the solution was allowed to warm to room

temperature over 1 h. The reaction mixture was acidified with 1 M HCl and 100 mL of ether was added. The aqueous layer was extracted with ether (3 × 50 mL) and the combined organic layer was washed with water, dried (MgSO₄), and concentrated to give the crude product, which was recrystallized from ethanol–water (1:4) to give 2-bromothiophene-3-carboxylic acid as an off white crystalline solid (2.11 g, 68%). Mp: 176–8 °C (lit.^{36,37} mp 178–9 °C). ¹H NMR: δ 9.7–10.5 (1H, v broad), 7.25 (1H, d, $J = 5.5$ Hz), 7.44 (1H, d, $J = 5.9$ Hz). ¹³C NMR: δ 122.1, 126.2, 129.9, 130.3, 167.2. IR: 702, 735, 831, 891, 999, 1189, 1295, 1432, 1450, 1526, 1683 cm⁻¹. Anal. Calcd for C₅H₃O₂SBr: C, 29.00; H, 1.46. Found: C, 29.05, H, 1.68.

General Procedure for Diazomethane Esterification of Thiophene Carboxylic Acids. The thiophene carboxylic acid (3 mmol) was dissolved in 20 mL of ether and cooled to 0 °C, and then 50 mL of a cold diazomethane (5 mmol) solution in ether³⁸ was added and allowed to warm to room temperature over 3 h. The solvent was removed under reduced pressure, leaving the methyl ester.

Methyl 2-bromothiophene-3-carboxylate (9)²² was prepared from 2-bromothiophene-3-carboxylic acid to yield a pale yellow oil in 100% yield. ¹H NMR: δ 3.87 (3H, s), 7.21 (1H, d, $J = 5.8$ Hz), 7.34 (1H, d, $J = 5.8$ Hz).

Methyl 2-bromothiophene-4-carboxylate (11)²² was prepared from 2-bromothiophene-4-carboxylic acid^{39,40} in 100% yield. Mp: 43–4 °C (lit.²² mp 43 °C). ¹H NMR: δ 3.85 (3H, s), 7.46 (1H, d, $J = 1.5$ Hz), 7.98 (1H, d, $J = 1.5$ Hz).

Methyl thiophene-3-carboxylate²² was prepared from thiophene-3-carboxylic acid as a colorless oil in 100% yield. ¹H NMR: δ 3.86 (3H, s), 7.30 (1H, dd, $J = 5.1, 3.2$ Hz), 7.52 (1H, dd, $J = 5.1, 1.2$ Hz), 8.10 (1H, dd, $J = 3.2, 1.2$ Hz).

General Procedure for the Synthesis of Dimethyl 2,2'-Bithiophene-4,4'-dicarboxylate (3) and Dimethyl 2,2'-Bithiophene-3,3'-dicarboxylate (5). The methyl 2-bromothiophenecarboxylate (2 mmol) was dissolved in 0.5 mL of dry DMF, copper powder (508 mg, 8.0 mg-atom) was added, and the mixture was heated at 145 °C under an argon atmosphere for 2 days. The reaction mixture was cooled, dissolved in 10 mL of CHCl₃, filtered, and dried (MgSO₄). The residue was chromatographed on silica gel, eluting with ethyl acetate:hexane (1:4) to give the bithiophene as a white powder.

Dimethyl 2,2'-bithiophene-4,4'-dicarboxylate (3) was prepared from 11 in 51% yield. Mp: 175–6 °C. ¹H NMR: δ 3.88 (6H, s), 7.58 (2H, d, $J = 1.4$ Hz), 8.00 (2H, d, $J = 1.4$ Hz). ¹³C NMR: δ 52.1, 124.7, 132.0, 134.2, 137.0, 162.8. IR (KBr): 740, 843, 867, 987, 1091, 1243, 1346, 1443, 1524, 1726 cm⁻¹. UV: λ_{\max} 304 (ϵ 7600), 233 nm (ϵ 25 000). Anal. Calcd for C₁₂H₁₀O₄S₂: C, 51.04; H, 3.57; S, 22.71. Found: C, 51.11; H, 3.40; S, 23.01. The sample for single-crystal X-ray crystallography was prepared by recrystallization from ethyl acetate:hexane (1:9).

Dimethyl 2,2'-bithiophene-3,3'-dicarboxylate (5) was prepared from 9 in 55% yield. Mp: 148–9 °C. ¹H NMR: δ 3.69 (6H, s), 7.34 (2H, d, $J = 5.4$ Hz), 7.52 (2H, d, $J = 5.4$ Hz). ¹³C NMR: δ 51.8, 125.9, 129.6, 131.3, 140.0, 163.2. IR (KBr): 744, 1002, 1156, 1247, 1286, 1433, 1722 cm⁻¹. UV: λ_{\max} 307 (ϵ 7000), 254 nm (ϵ 15 000). Anal. Calcd for C₁₂H₁₀O₄S₂: C, 51.04; H, 3.57; S, 22.71. Found: C, 51.32; H, 3.78; S, 22.61. The sample for single-crystal X-ray crystallography was prepared by recrystallization from ethyl acetate:hexane (1:9).

Dimethyl 2,2'-Bithiophene-3,4'-dicarboxylate (4). Methyl 2-(tri-*n*-butylstannyl)thiophene-3-carboxylate (10) was first

(36) Campaigne, E.; LeSuer, W. M. *J. Am. Chem. Soc.* **1949**, *71*, 333.

(37) Gronowitz, S.; Pettersson, K. *J. Heterocycl. Chem.* **1976**, *13*, 1099.

(38) Arndt, F. In *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 165.

(39) Campaigne, E.; Bourgeois, R. C. *J. Am. Chem. Soc.* **1954**, *76*, 2445.

(40) Cheng, Y. Ph.D. Dissertation, The University of Texas at Arlington, Arlington, TX, 1998.

(35) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapter 17.

prepared as follows. To a solution of diisopropylamine (1.01 g, 10 mmol) in 10 mL of dry tetrahydrofuran at $-78\text{ }^{\circ}\text{C}$ was added *n*-butyllithium (6.5 mL of a 1.53 M solution in hexane, 10 mmol) under an argon atmosphere. After stirring for 25 min, a solution of methyl thiophene-3-carboxylate (1.42 g, 10 mmol) in 10 mL of dry tetrahydrofuran was added slowly over 10 min, the mixture was allowed to stand at $-78\text{ }^{\circ}\text{C}$ for an additional 20 min, and then tri-*n*-butylstannyl chloride (2.98 mL, 3.57 g, 11 mmol) was added, by syringe, all at once. The cooling bath was removed, and the solution was allowed to warm to room temperature over 3 h, after which 100 mL of saturated NaCl solution was added, followed by extraction with methylene chloride ($3 \times 20\text{ mL}$). Triethylamine (4 mL) was added to the combined organic layer, which was dried and concentrated to give **10** as a pale yellow oil, which was used in the next step. $^1\text{H NMR}$: δ 0.8–1.3 (21H, m), 1.52 (6H, m), 3.84 (3H, s), 7.53 (1H, d, $J = 5.8\text{ Hz}$), 7.66 (1H, d, $J = 5.8\text{ Hz}$). IR (film): 713, 832, 877, 961, 1073, 1147, 1193, 1255, 1366, 1462, 1517, 1705, 2958 cm^{-1} . Methyl 2-bromothiophene-4-carboxylate (**11**, 332 mg, 1.5 mmol) and **10** (647 mg, 1.5 mmol) were dissolved in 2.5 mL of dry toluene. Copper(I) iodide (29 mg, 0.15 mmol) and tetrakis(triphenylphosphine)palladium(0) (87 mg, 0.075 mmol) were added, and the mixture was refluxed under argon for 20 h. The reaction mixture was cooled, treated with 1 mL of 10% sodium fluoride, diluted with 20 mL of CHCl_3 , and filtered. The resulting solution was concentrated and the residue was chromatographed on silica gel, eluting with ethyl acetate:hexane (1:4) mixture to yield 173 mg (52%) of **4** as a white crystalline powder. Mp: $167\text{--}8\text{ }^{\circ}\text{C}$. $^1\text{H NMR}$: δ 3.83 (3H, s), 3.87 (3H, s), 7.23 (1H, d, $J = 5.5\text{ Hz}$), 7.44 (1H, d, $J = 5.5\text{ Hz}$), 7.76 (1H, d, $J = 0.9\text{ Hz}$), 8.15 (1H, d, $J = 0.9\text{ Hz}$). $^{13}\text{C NMR}$: δ 51.9, 52.0, 124.7, 128.2, 129.4, 130.5, 133.1, 134.6, 134.7, 142.1, 163.0, 163.4. IR (KBr): 725, 740, 755, 833, 846, 988, 1008, 1150, 1208, 1265, 1366, 1531, 1716, 1719 cm^{-1} . UV: λ_{max} 313 (ϵ 13 000), 248 nm (ϵ 22 000). Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$: C, 51.04; H, 3.57; S 22.71. Found: C, 51.28; H, 3.41; S, 22.88. The sample for single-crystal X-ray crystallography was prepared by recrystallization from ethyl acetate:hexane (1:9).

X-ray Structure Determination. Data collections were carried out at room temperature on a Siemens P4 diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation. The unit cell parameters of **3**, **4**, and **5** were determined by least squares refinement of 41, 40, and 38 reflections, respectively. The data were corrected for Lorentz, polarization, and absorption effects. Structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement on F^2 and difference Fourier analysis. All non-hydrogen atoms were refined anisotropically. Compound

TABLE 6. Crystal Data and Summary of Data Collection and Refinement for Compounds 3, 4, and 5

	3	4	5
formula	$\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$	$\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$	$\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_2$
fw	282.32	282.32	282.32
space group	$C2/c$	$P\bar{1}$	$C2$
T , K	298(2)	298(2)	298(2)
λ , Å	0.71073	0.71073	0.71073
a , Å	28.118(7)	4.8597(11)	13.9359(15)
b , Å	3.8921(10)	9.7725(15)	6.3413(10)
c , Å	11.034(3)	13.6317(15)	8.8327(9)
α , deg	90	70.857(10)	90
β , deg	96.15(3)	84.911(13)	124.263(9)
γ , deg	90	86.175(13)	90
V , Å ³	1200.6(6)	608.69(18)	645.10(14)
Z	4	2	2
ρ (calc), g/cm^3	1.562	1.540	1.453
μ , mm^{-1}	0.446	0.440	0.415
R1, wR2 [$I > 2\sigma(I)$] ^a	0.0280, 0.0750	0.0306, 0.0755	0.0258, 0.0685
R1, wR2 (all data) ^a	0.0313, 0.0768	0.0341, 0.0780	0.0268, 0.0692

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

3 crystallizes in the $C2/c$ space group with a crystallographically imposed center of symmetry at the middle of the C2–C2A bond. Compound **5** crystallizes in the $C2$ space group with a crystallographically imposed 2-fold rotation axis on the C2–C2A bond. All the hydrogen atoms of **3** and **4** and thiophene ring hydrogens of **5** were located from the difference map and refined isotropically. The methyl hydrogen atoms of **5** were included at calculated positions. Tables 4–6 show structural parameters for **3–5**.

Software programs and the sources of scattering factors are contained in the Bruker SHELXTL 5.1 software package provided by the Bruker Analytical X-ray Instruments, Inc. Some details of data collection and refinements are given in Table 6.

Acknowledgment. We thank the Robert A. Welch Foundation (Grants Y-1407 and Y-1289) for support of this work.

Supporting Information Available: Full details of the X-ray structures of **3**, **4**, and **5**, including the complete tables of crystal data, atomic coordinates, bond lengths and angles, positional and anisotropic thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO020307B