# 3,3';2',2";3",3'"-TETRATHIOPHENE: SYNTHESIS AND CRYSTAL STRUCTURE

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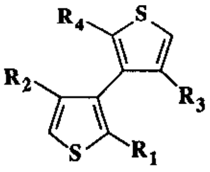
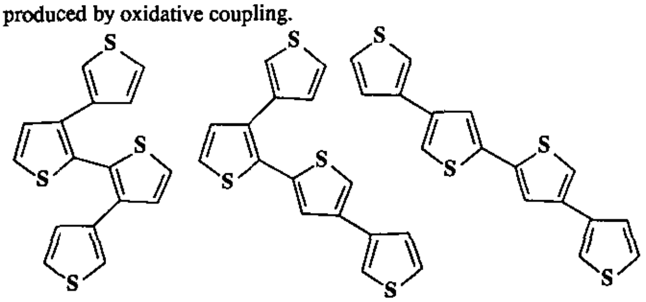
Abstract — The title structure was obtained from X-ray data on the product formed when the monolithio derivative of 3,3'-bithienyl was treated with $CuCl_2$. The thiophene rings were not coplanar: the angle between adjacent rings was about 20° in the 3,3'-bithienyl moieties, and 110° in the 2,2'-bithienyl moiety. The product was best formed (in 84% yield) by coupling 2-bromo-3,3'-bithienyl with its Grignard derivative by the Kumada procedure.

Very little is known about thiophene oligomers possessing either beta linkages or alternating alpha and beta linkages. X-ray data have been recorded for the 2,2'- and 3,3'-bithienyls, which are planar.[2,3] Substitution may lead to restricted rotation, and several 3,3'-bithienyls with large substituents adjacent to the rings' junction were obtained in optically active form. X-ray crystallographic data were reported for **5**[4] and **6**[5], which are not planar. One crystallographic study of large alpha-thiophene oligomers has appeared,[6] but was not detailed enough for deducing bond angles or bond lengths. No other polythiophenes seem to have been analyzed crystallographically.

The two pairs of different alpha hydrogens in **1** should lead to two different monolithio derivatives, from which three isomeric tetrathiophenes, **2**, **3**, and **4**, could be produced by oxidative coupling.





**1** $R_1 = R_2 = R_3 = R_4 = H$ **2** **3** **4**

**5** $R_1 = R_3 = CH_3$, $R_2 = R_4 = COOH$

**6** $R_1 = R_3 = H$, $R_2 = COOCH_3$, $R_4 = Br$

Both lithio derivatives were formed even when 0.5 equiv. of base was used (either n-butyllithium or lithium diisopropylamide), as judged by the carboxylation of the initial reaction mixture, which gave mixtures of mono- and dicarboxylic acids. However, a single dimeric product was obtained in 6% yield when **1** was treated with 1 equiv. of n-BuLi, followed by $CuCl_2$. Its structure determination by nmr was not conclusive, but X-ray analysis of one crystal proved it to be **2**. The yield of **2** was improved to 40% by halogen–metal exchange on 2-bromo-3,3'-bithienyl, treated with 1 equiv. of n-butyllithium. However, Kumada's procedure[2] proved to be best: coupling of 2-bromo-3,3'-bithienyl with 1 equiv. of the corresponding Grignard reagent in the presence of $Ni(dppp)Cl_2$ produced the tetrathiophene **2** in 84% yield [dppp = 1,3-bis(diphenylphosphino)propane].

### The Structure of 2.

There is a two-fold symmetry axis in 2, passing through the midpoint of $C_1$ and $C'_1$ and that of $C_{10}$ and $C'_{10}$ (Fig. 1). The bond lengths and bond angles (Tables 1 and 2) are in good agreement with those of simpler thiophenes. Although each thiophene ring is planar, the molecule is not. The dihedral angles are 20.3° between the planes of one internal thiophene and the adjacent terminal thiophene, and 109.4° between the planes of the two internal rings. The fact that the four thiophene rings are not in the same plane is also reflected in the ultraviolet spectrum. As expected for a molecule in which the two connected 3,3'-bithienyl units are almost orthogonal, the absorption maximum of 262 nm (ε 20,200) is not very different from that of 3,3'-bithienyl (253 nm, ε 14,300). It is rather different from that of 2,2'-bithienyl (301 nm, ε 12,900).

An interesting phenomenon was also observed. In the plane of the terminal thiophene rings two orientations of the sulfur coexisted, in the ratio of about 2 to 1. Thus, there were three isomers present in the crystal, as shown in Fig. 2. The atoms $S_D$ and $C_D$ (Fig. 1) are disordered, with sulfur and carbon contributions $S_D = 0.63S + 0.37C$, and $C_D = 0.63C + 0.37S$. The contributions were determined by refining the occupancies of these two atoms as sulfur, with an isotropic temperature factor $B = 4\ A^2$. From these occupancies, the relative contributions were calculated. Subsequent refinements of the anisotropic temperature factors were performed for the two atoms, with structural factors based on these relative weights (Table 5).

## EXPERIMENTAL

Synthesis of 2 (method A). To a solution of 3,3'-bithienyl (0.513 g, 3.1 mmol) in 50 ml of THF cooled to –78 °C was added 1.2 ml of 2.5 M n-BuLi (3 mmol) in hexane under $N_2$. After 1 h at –78 °C, a solution of $CuCl_2$ (0.40 g, 3 mmol) in 10 ml of DMF was added. The mixture was stirred for 1 h at –78 °C, and overnight at room temp. It was quenched with 25 ml of 3% HCl, extracted with ether (3 × 25 ml), which was then washed with water, dried over $MgSO_4$, and concentrated. The residue was flash chromatographed over silica gel using hexane (yielding 160 mg of starting material) and hexane/EtOAc. A white crystalline material (30 mg) was obtained from the fractions eluted with 1% EtOAc in hexane; mp 169.5-171.5 °C; mass spec 330 ($M^+$, 100%); NMR, 6.92 (dd, 1 H), 7.00 (dd, 1H), 7.14 (dd, 1 H), 7.24 (d, J = 5.3 Hz, 1 H), 7.39 (d, J = 5.2 Hz, 1 H): $^{13}C$ NMR, 121.92, 124.97, 126.48, 127.16, 128.46, 129.02, 136.11, 136.53 ppm; UV (EtOH) 262 nm (ε 20,200). Crystals suitable for X-ray analysis were obtained by slow evaporation of a hexane solution at room temperature.

Method B. To a solution of 2-bromo-3,3'-bithienyl (3.0 g, 12.24 mmol) in 50 ml of ether at –78 °C under $N_2$ was added 4.9 ml of 2.5 M n-BuLi (12.25 mmol) in hexane. After 10 min a white suspension was present. Anhydrous $CuCl_2$ (2.0 g, 14.9 mmol) was added and stirred for 5 min at –78 °C. The mixture was allowed to reach room temp, and was refluxed overnight. After quenching with 25 ml of 3 M HCl, the solid was filtered off. It was dissolved in hot heptane and filtered through a short silica gel column. Recrystallization twice from heptane gave 0.562 g of 2, as slightly colored crystals, mp 167–170.5 °C. The ether phase was washed with water and satd NaCl, dried over $MgSO_4$, and concentrated. The residue was flash chromatographed using hexane:acetone (49:1) to yield 0.403 g of slightly impure **2**, which was recrystallized from heptane and gave 0.246 g of **2** as slightly colored crystals, mp 168-171.5 °C (total yield 40%).

Method C. A mixture of 2-bromo-3,3'-bithienyl (280 mg, 1.14 mmol), 1,2-dibromoethane (300 mg, 1.6 mmol) and Mg turnings (300 mg, 12.3 mmol) in 25 ml of ether was refluxed for 2.5 h. The Grignard reagent was added to a mixture of 2-bromo-3,3'-bithienyl (200 mg, 0.82 mmol) and 5 mg of $Ni(dppp)Cl_2$ in 10 ml of ether, refluxed for 48 h, and quenched with 10 ml of 2 M HCl. After addition of enough $CH_2Cl_2$ to dissolve the solid formed, the organic layer was separated, washed with satd NaCl, dried, and concentrated. The residue was dissolved in boiling ligroin (bp 94-105 °C) and filtered through a short silica gel column. The solution was concentrated and cooled. It gave 256 mg of yellow solid, which was recrystallized from EtOH and yielded 226 mg (84%) of **2**, mp 166-170 °C, which showed a single spot on tlc.

**Crystal Data.** $C_{16}H_{10}S_4$, M = 331.2. Tetragonal, a = 7.177(2), c = 28.334(9) A, V = 1459.6 $A^3$, space group $P4_33_12$ (No 96) Z = 4. Colorless, crystal dimensions 0.20 × 0.20 × 0.20 mm.

Data Collection and Processing. C4D4 diffractometer, ω-θ mode with ω scan width 0.80 + 0.35 tan θ, ω scan speed 1.37—8.24 deg $min^{-1}$, graphite-monochromated Mo K radiation; 1308 reflections were measured (1° ≤ θ ≤ 23°, h, k, l), giving 485 with I > 3σ (I). Linear and approx. isotropic crystal decay, ca 0.6%. No absorption correction was done.

Structure Analysis and Refinement. Direct methods. Full-matrix least squares refinements with all non-hydrogen atoms anisotropic and hydrogen participating in Fc calculations only. Unit weighting scheme; final $R_1$ and $R_2$ values were 0.021 and 0.022. SDP and MICROVMS were used. The final atomic positional and thermal parameters and their estimated standard deviations are listed in Tables 3 and 4, respectively.

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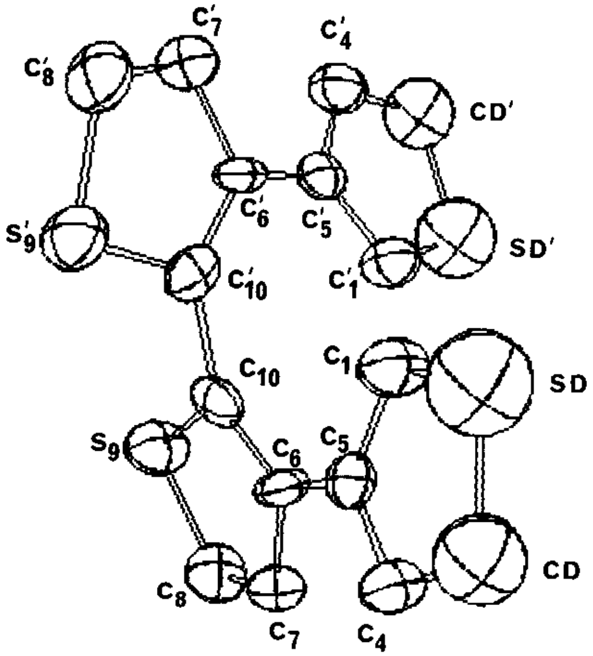

FIGURE 1. Structure of **2**.

TABLE 1.Bond Distances in Angstroms

| Atom 1 | Atom 2 | Distances |
|---|---|---|
| C1 | SD | 1.606(7) |
| C1 | C5 | 1.393(8) |
| SD | CD | 1.707(5) |
| CD | C4 | 1.550(7) |
| C4 | C5 | 1.411(9) |
| C5 | C6 | 1.449(8) |
| C6 | C7 | 1.435(8) |
| C6 | C10 | 1.357(8) |
| C7 | C8 | 1.325(9) |
| C8 | S9 | 1.706(7) |
| S9 | C10 | 1.731(6) |
| C10 | C10' | 1.508(8) |

Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 2. Bond Angles in Degrees

| Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|
| SD | C1 | C5 | 116.4(5) |
| C1 | SD | CD | 98.5(3) |
| SD | CD | C4 | 101.7(3) |
| CD | C4 | C5 | 116.3(5) |
| C1 | C5 | C4 | 107.1(5) |
| C1 | C5 | C6 | 125.4(5) |
| C4 | C5 | C6 | 127.4(5) |
| C5 | C6 | C7 | 123.2(5) |
| C5 | C6 | C10 | 126.5(5) |
| C7 | C6 | C10 | 110.2(5) |
| C6 | C7 | C8 | 114.2(5) |
| C7 | C8 | S9 | 112.2(5) |
| C8 | S9 | C10 | 90.9(3) |
| C6 | C10 | S9 | 112.4(4) |
| C6 | C10 | C10' | 129.9(5) |
| S9 | C10 | C10' | 117.7(4) |

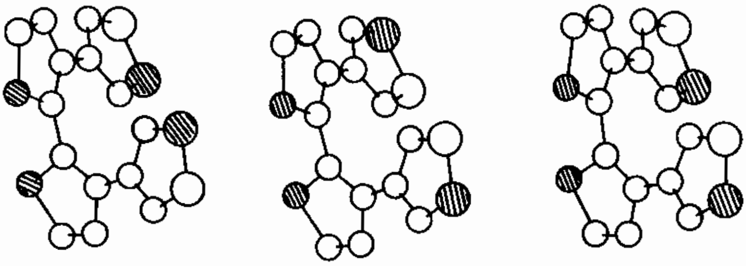

FIGURE 2. The three isomeric forms of 2 (the sulfur atoms are shaded).

TABLE 3. Positional Parameters and Their Estimated Standard Deviations

| Atom | x | y | z | B(A2) |
|---|---|---|---|---|
| C1 | 0 1512(9) | −0.2074(9) | 0.3866(2) | 3.8(2) |
| SD | −0.0116(4) | −0.2263(4) | 0.34802(9) | 6.39(6) |
| CD | −0.1806(5) | −0.1043(5) | 0.3769(1) | 8.4(1) |
| C4 | −0.0774(9) | −0.0446(9) | 0.4225(2) | 3.7(1) |
| C5 | 0.1092(8) | −0.1041(8) | 0.4269(2) | 2.7(1) |
| C6 | 0.2369(7) | −0.0653(7) | 0.4652(2) | 2.5(1) |
| C7 | 0.4038(9) | −0.1706(8) | 0.4734(2) | 3.5(1) |
| C8 | 0 5044(9) | −0.1111(9) | 0.5096(2) | 4.1(2) |
| S9 | 0.4094(2) | 0 0807(3) | 0.53580(6) | 3.95(3) |
| C10 | 0.2222(7) | 0.0744(8) | 0.4973(2) | 2.8(1) |
| H1 | 0.2698 | −0.2634 | 0.3822 | 4.9* |
| H4 | −0.1364 | 0.0280 | 0.4462 | 4.8* |
| H7 | 0.4391 | −0.2739 | 0.4544 | 4.5* |
| H8 | 0.6165 | −0.1686 | 0.5198 | 5.3* |

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as· (4/3) × [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

TABLE 4. General Displacement Parameter Expressions—U's

| Atom | U(1,1) | U(2,2) | U(3,3) | U(1,2) | U(1,3) | U(2,3) |
|---|---|---|---|---|---|---|
| C1 | 0.051(4) | 0.040(4) | 0.054(4) | 0.004(4) | 0.012(3) | −0.007(4) |
| SD | 0.079(2) | 0.085(2) | 0.079(1) | −0.009(2) | −0.002(2) | −0.021(2) |
| CD | 0.115(3) | 0.095(3) | 0.108(2) | 0.007(2) | −0.012(2) | −0.020(2) |
| C4 | 0.046(4) | 0.050(4) | 0.045(3) | 0.007(4) | 0.005(4) | −0.008(3) |
| C5 | 0.040(3) | 0.023(3) | 0.040(3) | −0.001(3) | 0 008(3) | 0.008(3) |
| C6 | 0.030(3) | 0.027(2) | 0.039(3) | 0 010(3) | 0.002(3) | −0.009(3) |
| C7 | 0.038(4) | 0.040(3) | 0.053(4) | 0.006(3) | 0.006(4) | −0.004(3) |
| C8 | 0.039(3) | 0.054(4) | 0.062(4) | 0.005(4) | −0.014(3) | 0.008(4) |
| S9 | 0.0387(8) | 0.0596(9) | 0.0518(7) | 0.005(1) | −0.009(1) | −0.009(1) |
| C10 | 0.031(3) | 0 040(3) | 0.034(3) | −0.000(3) | −0.011(3) | 0.013(3) |

The form of the anisotropic displacement parameter is:
exp[−2P12{h2a2U(1,1) + k2b2U(2,2) + 12c2U(3,3) + 2hkabU(1,2) + 2h1acU(1,3) + 2k1bcU(2,3)}], where a, b, and c are reciprocal lattice constants.

TABLE 5. General Displacement Parameter Expressions—B's

| Atom | B(1,1) | B(2,2) | B(3,2) | B(1,2) | B(1,3) | B(2,3) | Beqv |
|---|---|---|---|---|---|---|---|
| C1 | 4.0(3) | 3.1(3) | 4.3(3) | 0.3(3) | 1.0(3) | −0.5(3) | 3.8(2) |
| SD | 6.2(1) | 6.7(1) | 6.2(1) | −0.7(1) | −0.1(1) | −1.7(1) | 6.39(6) |
| CD | 9.1(2) | 7.5(2) | 8.5(2) | 0.6(2) | −0.9(2) | −1.6(2) | 8.4(1) |
| C4 | 3.7(3) | 3.9(3) | 3.6(3) | 0.6(3) | 0.4(3) | −0.6(3) | 3.7(1) |
| C5 | 3.2(3) | 1.8(2) | 3.2(2) | −0.1(3) | 0.6(3) | 0.6(2) | 2.7(1) |
| C6 | 2.3(3) | 2.2(2) | 3.1(2) | 0.8(2) | 0.1(3) | −0.7(2) | 2.5(1) |
| C7 | 3.0(3) | 3.2(3) | 4.2(3) | 0.5(3) | 0.4(3) | −0.3(2) | 3.5(1) |
| C8 | 3.1(3) | 4.3(3) | 4.9(3) | 0.4(3) | −1.1(3) | 0.6(3) | 4.1(2) |
| S9 | 3.06(6) | 4.70(7) | 4.09(6) | 0.43(8) | −0.73(8) | −0.74(8) | 3.95(3) |
| C10 | 2.5(2) | 3.2(3) | 2.7(2) | −0.0(2) | 0.9(2) | 1.1(3) | 2.8(1) |

The form of the anisotropic displacement parameter is·
exp[−0.25{h2a2B(1,1) + k2b2B(2,2) + 12c2B(3,3) + 2hkabB(1,2) + 2h1acB(1,3) + 2k1bcB(2,3)}], where a, b, and c are reciprocal lattice constants.

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