SYNTHESIS OF HIGHLY CONGESTED BI- AND TERTHIOPHENES; 3,4,3',4'-TETRA-*tert*-BUTYLBITHIOPHENE AND 3',4'-DI-*tert*-BUTYL-2,2':5',2"-TERTHIOPHENE

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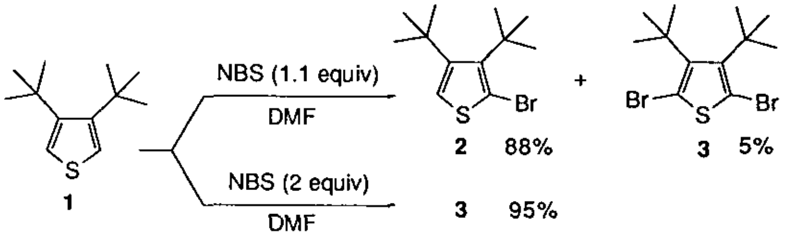
Abstract- The $Pd(PPh_3)_4$-catalyzed coupling of 3,4-di-*tert*-butyl-2-thienylmagnesium bromide with 2-bromo-3,4-di-*tert*-butylthiophene gave 3,4,3',4'-tetra-*tert*-butyl-2,2'-bithiophene (**5**) in moderate yield. X-Ray single crystal structure analysis of **5** revealed that its thiophene rings remain planer, but their plane is perpendicular to each other. The synthesis of 3',4'-di-*tert*-butyl-2,2':5',2"-terthiophene in a similar way is also described.

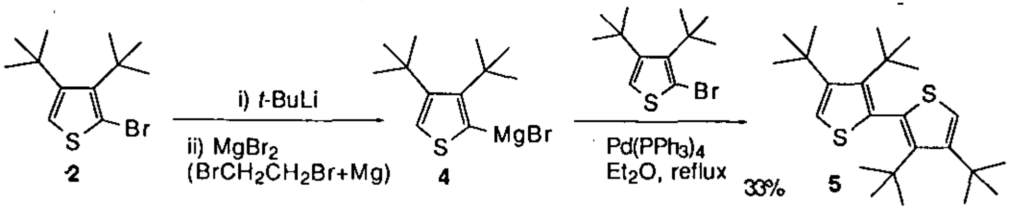
We have been investigating the synthesis of highly congested thiophenes[1] and synthesis of thiophene oligomers.[2] Recently, in connection with the investigation on the structural defects of polythiophenes and their alkyl derivatives as electronic devices, the rotational isomerization between individual thiophene rings in thiophene oligomers has been examined in some detail.[3] In this connection, we have now become interested in the preparation of highly congested thiophene oligomers. Here we report the preparation of bi- and terthiophenes carrying two *tert*-butyl groups on adjacent position.

Dedicated to Professor Shigeru Oae on the occasion of his 77th birthday.

We have developed a convenient synthesis of 3,4-di-*tert*-butylthiophene (**1**).[1a] Bromination of **1** with a slight excess of NBS (*N*-bromosuccinimide) in DMF gave 2-bromo-3,4-di-*tert*-butylthiophene (**2**) and 2,5-dibromo-3,4-di-*tert*-butylthiophene (**3**) in 88% and 5% yields, respectively.[4] Bromination of **1** with 2 molar amounts of NBS gave **3** in 95% yield.

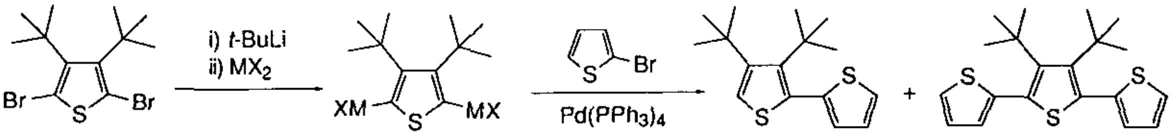


After much effort, it proved that the synthesis of 3,4,3',4'-tetra-*tert*-butyl-2,2'-bithiophene (**5**) by reductive coupling of **2** using a nickel catalyst (prepared by reduction of $NiCl_2$ with zinc powder in the presence of PPh_3), the method useful for the preparation of a series of thiophene oligomers,[2b] was unsuccessful probably because of steric reasons. We therefore examined the synthesis of **5** by coupling of **2** with 3,4-di-*tert*-butyl-2-thienylmagnesium bromide (**4**). Because **2** is inert to magnesium and thus **4** could not be obtained from **2** directly, it was prepared by treatment of **2** with *tert*-BuLi and then with $MgBr_2$ (prepared from 1,2-dibromoethane and magnesium). The coupling of **2** with **4**, catalyzed by $Pd(PPh_3)_4$,[5] in refluxing ether for 18 h gave the expected bithiophene (**5**)[6] in 33% yield.



Next we have examined the preparation of 3',4'-di-*tert*-butyl-2,2':5',2''-terthiophene (**8**). The attempted synthesis of **8** by $Pd(PPh_3)_4$-catalyzed coupling of the dibromide (**3**) with 2 molecules of 2-thienylmagnesium bromide did not give any amount of **8**; halogen-metal exchange between **3** and 2-thienylmagnesium bromide resulted in the formation of 2,2'-

bithiophene and 2-bromo-3,4-di-*tert*-butylthiophene as the major products. We then prepared the bis-Grignard reagent (**6a**) by treatment of the dibromide (**3**) with 4 molar amounts of *tert*-BuLi and then with $MgBr_2$. The $Pd(PPh_3)_4$-catalyzed coupling of **6a** with 2-bromothiophene in refluxing ether, however, also failed to give the expected terthiophene (**8**), but gave 3,4-di-*tert*-butyl-2,2'-bithiophene (**7**)[6] in 34% yield. We have then prepared the zinc reagent (**6b**) by treatment of **3** with *tert*-BuLi and then with $ZnCl_2$.[7] The $Pd(PPh_3)_4$-catalyzed coupling of **6b** with 2-bromothiophene in refluxing tetrahydrofuran satisfactorily gave the expected terthiophene (**8**)[6] in 43% yield along with the bithiophene (**7**) in 42% yield, although the reaction in reflxuing ether gave **8** and **7** only in 3% and 14% yields, respectively.



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6a : MX = MgBr
6b: MX =ZnCl

MX	solvent	**7**	**8**
MgBr	Et_2O	34%	0%
ZnCl	Et_2O	14%	3%
ZnCl	THF	42%	43%

The bithiophenes (**5**) and (**7**) are both colorless crystalline compounds. Their uv-vis spectra are given in Figure 1 along with those of 2,2'-bithiophene. The longest λ_{max} of **5** and **7** appear at 248.5 (ε 8320) and 247 nm (12400), respectively. The more congested bithiophene (**5**) has a smaller ε_{max} value than that of **7**. The position of λ_{max} of these compounds is rather close to that of 3,4-di-*tert*-butylthiophene (**1**) (λ_{max} 238.5 nm). 2,2'-Bithiophene has two absorption maxima at 248 and 306 nm. The latter longer absorption is not observed with **5** and **7**. These facts indicate that two thiophene rings of **5** and **7** are far from coplanar because of steric hindrance caused by bulky *tert*-butyl groups and thus do not conjugate each other. The terthiophene (**8**) is a colorless crystalline compound, while unsubstituted 2,2':5',2"-terthiophene is a yellow one. Thus, λ_{max} of **8** appears at 242 nm (ε 15100) with a shoulder at *ca.* 270 nm (11700), while those of the unsubstituted terthiophene appear at 252 and 353 nm (ε 7220 and 19300, respectively) (Figure 2). These observations also lead to the conclusion that no conjugation takes place between thiophene rings of **8**.

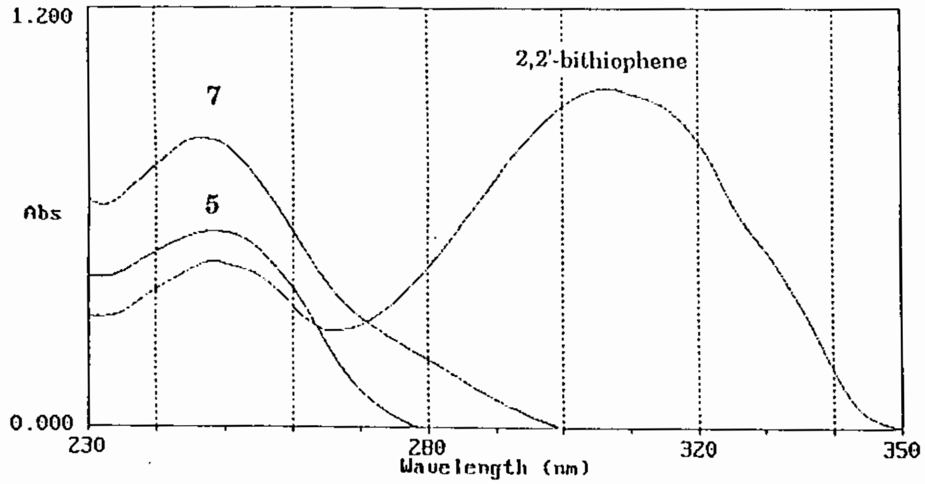

Figure 1. Uv-Vis Spectra of **5**, **7**, and 2,2'-Bithiophene (CH_2Cl_2 as the solvent)

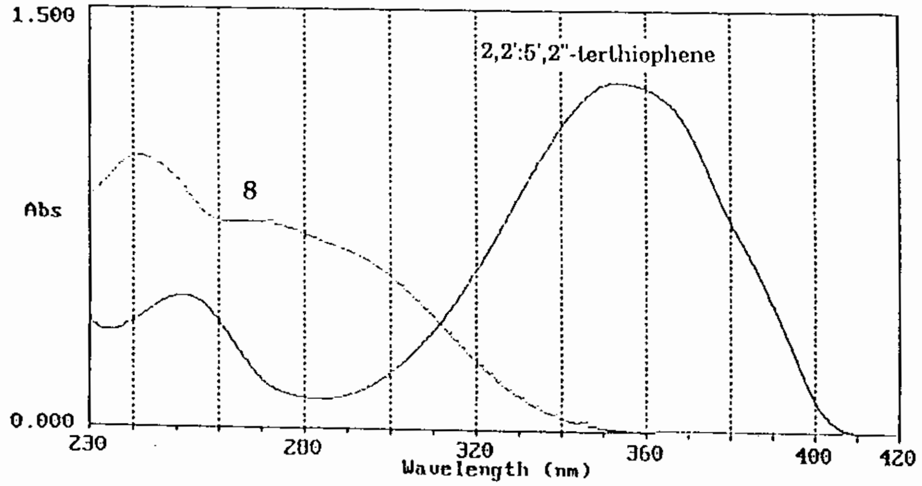

Figure 2. Uv-Vis Spectra of **8** and 2,2':5',2''-Terthiophene (CH_3CN as the solvent)

Figure 3 shows an ORTEP drawing structure of the bithiophene **5**.[8] Two thiophene rings of **5** are almost perpendicular to each other; S1-C1-C2-S2 torsion angle is 89.2(3)°. This observation is in harmony with the result by uv-vis spectra. The thiophene rings still remain nearly planar; two *tert*-butyl groups are twisted with torsion angles of 9.9 and 8.5°. Relevant bond lengths and bond angles data are given in Figure 4.

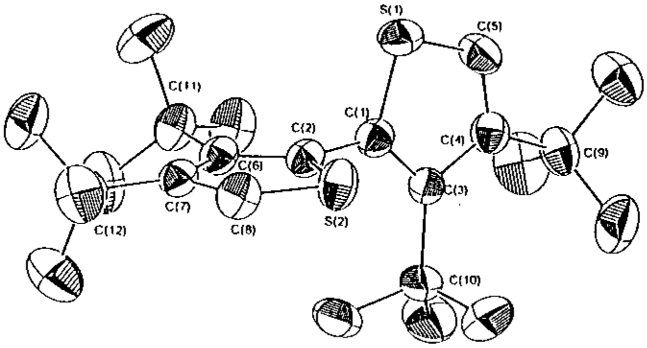

Figure 3. An ORTEP Drawing Structure of **5**

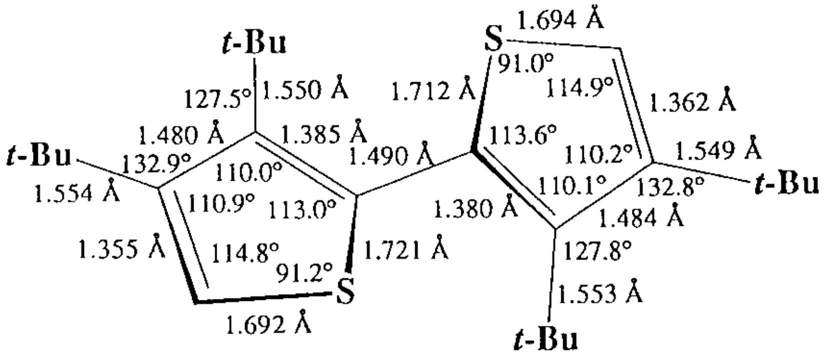

Figure 4. Relevant Bond Lengths and Bond Angles Data of **5**

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. a) J. Nakayama, S. Yamaoka, and M. Hoshino, *Tetrahedron Lett.*, 1988, **29**, 1161. b) J. Nakayama and R. Hasemi, *J. Am. Chem. Soc.*, 1990, **112**, 5654. c) J. Nakayama and K. Yoshimura, *Tetrahedron Lett.*, 1994, **35**, 2709.

2. a) J. Nakayama, Y. Nakamura, S. Murabayashi, and M. Hoshino, *Heterocycles*, 1987, **26**, 939. b) J. Nakayama, T. Konishi, S. Murabayashi, and M. Hoshino, *Heterocycles*, 1987, **26**, 1793. c) J. Nakayama, S. Murabayashi, and M. Hoshino, *Heterocycles*, 1987, **26**, 2599.

3. J. C. Horne, G. B. Blanchard, and E. LeGoff, *J. Am. Chem. Soc.*, 1995, **117**, 9571 and references cited therein.

4. The use of DMF as the solvent enables **2** to be prepared more selectively compared with bromination in a mixture of AcOH and CH_2Cl_2.[1a]

5. A. Minato, K. Suzuki, K. Tamao, and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1984, 511.

6. **5**: mp 171.5-172.5 °C; colorless needles (from hexane); ^{1}H-nmr ($CDCl_3$, 400 MHz) δ 1.39 (18H, CH_3, s), 1.51 (18H, CH_3, s), 7.21 (2H, ring protons, s); ^{13}C-nmr ($CDCl_3$, 100 MHz) δ 33.7 (CH_3), 34.3 (CH_3), 36.5 (C), 36.9 (C), 122.1, 134.9, 146.0, 151.1 (ring carbons); ir (KBr) 3012, 2956, 1490, 1464, 1392, 1364, 1226, 1194, 954, 934, 924, 906, 758, 730 cm^{-1}; ms *m/z* 390 (M^+), 333, 319, 277, 263, 221. Anal. Calcd for $C_{24}H_{38}S_2$: C, 73.85; H, 9.74. Found: C, 74.03; H, 9.86. **7**: mp 85-86 °C, colorless needles (from EtOH); ^{1}H-nmr ($CDCl_3$, 400 MHz) δ 1.40 (9H, CH_3, s), 1.53 (9H, CH_3, s); ^{13}C-nmr ($CDCl_3$, 100 MHz) δ 33.9 (CH_3), 34.3 (CH_3), 36.2 (C), 36.7 (C), 122.6, 125.9, 126.2, 128.7, 131.2, 140.6, 148.5, 151.8 (ring carbons); ms *m/z* 278 (M^+), 263, 207, 206. Anal. Calcd for $C_{18}H_{22}S_2$: C, 69.01; H, 7.96. Found: C, 68.90; H, 8.00. **8**: mp 171-171.5 °C, colorless needles (from ethanol); ^{1}H-nmr ($CDCl_3$, 400 MHz) δ 1.46 (9H, CH_3, s), 6.96-7.02 (4H, m), 7.29-7.32 (2H, quasi-d); ^{13}C-nmr ($CDCl_3$, 100 MHz) δ 34.6 (CH3), 37.6 (C), 126.2, 126.7, 128.2, 131.2, 139.9, 150.1 (ring carbons); ms *m/z* 360 (M^+), 345, 304, 289. Anal. Calcd for $C_{20}H_{24}S_3$: C, 66.62; H, 6.71. Found: C, 66.76; H, 6.72 .

7. E.-I. Negishi, T. Takahashi, and A. O. King, *Org. Synth.*, 1993, Coll. Vol., 8, 430.

8. Crystal data for **5**: $C_{24}H_{38}S_2$, M = 390.70, monoclinic, space group *Pc* (no. 7), a = 9.068(5), b = 10.656(4), c = 12.209(6) Å, β = 99.89(4)°, V = 1162.0(10) Å^3, Z = 2, D_c = 1.12 gcm^{-3}, μ = 2.245 cm^{-1}, crystal size 0.30 x 0.20 x 0.20 mm, Mo-$K\alpha$ (λ = 0.71073 Å) , R = 0.0433 and R_w = 0.0453 for 2211 unique reflections.

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