

A NONPLANAR THIOPHENE, 3,4-DI-*tert*-BUTYL-2,5-BIS(TRIISOPROPYLSILYL)THIOPHENE

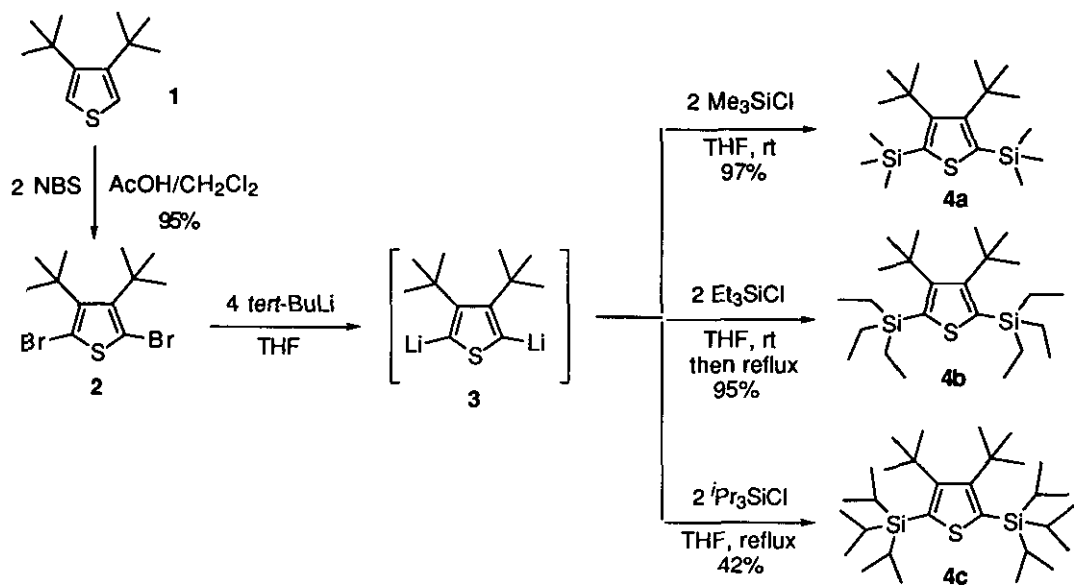
Juzo Nakayama,* Ting Yu, Yoshiaki Sugihara, Akihiko Ishii,
and Shigekazu Kumakura

Department of Chemistry, Faculty of Science, Saitama University,
Urawa, Saitama 338, Japan

Abstract - Treatment of 2,5-dibromo-3,4-di-*tert*-butylthiophene with *tert*-butyllithium followed by reaction with triisopropylsilyl chloride gave a highly congested thiophene, 3,4-di-*tert*-butyl-2,5-bis(triisopropylsilyl)thiophene, whose thiophene ring is no longer planar.

We have been investigating the syntheses, structures and reactions of congested thiophenes such as 3,4-di-*tert*-butyl-,^{1a-c} 2,3-di-*tert*-butyl-,^{1d} 3,4-di-1-adamantyl-,^{1e} and 3,4-dineopentylthiophenes.^{1f} The most congested tetrasubstituted thiophene ever synthesized would be tetra-*tert*-butylthiophene whose thiophene ring is no longer planar.² We have now planned to prepare another series of nonplanar tetrasubstituted thiophenes by introducing trialkylsilyl groups into the 2- and 5-positions of 3,4-di-*tert*-butylthiophene (**1**). We report here the preparation of 3,4-di-*tert*-butyl-2,5-bis(triisopropylsilyl)thiophene (**4c**) whose thiophene ring is nonplanar.

The thiophene **1**, now became readily obtainable in large quantities,^{1a,3} was brominated with 2 molar amounts of *N*-bromosuccinimide to give 2,5-dibromo-3,4-di-*tert*-butylthiophene (**2**) in 95% yield. Treatment of **2** with 4 molar amounts of *tert*-butyllithium in THF gave a suspension of 3,4-di-*tert*-butyl-2,5-dilithiothiophene (**3**). Preparation of **3** by dilithiation of **1** with alkylolithiums or lithium diisopropylamide was unsuccessful probably because of steric hindrance. Heating the suspension of **3** with triisopropylsilyl chloride at reflux for 24 h gave the desired product, 3,4-di-*tert*-butyl-2,5-bis(triisopropylsilyl)thiophene (**4c**), in 42% yield. Less congested thiophenes, 3,4-di-*tert*-butyl-2,5-bis(trimethylsilyl)thiophene (**4a**) and 3,4-di-*tert*-butyl-2,5-bis(triethylsilyl)thiophene (**4b**), were obtained more easily in much better yields. Thus, the reaction of **3** with trimethylsilyl chloride at room temperature gave **4a** in 97% yield, while the reaction with triethylsilyl chloride required refluxing for the completion to give **4b** in 95% yield. In the latter synthesis, the use of triethylsilyl trifluoromethanesulfonate gave **4b** in a decreased yield (34%).



All of **4** gave spectroscopic data⁴ and elemental analyses which are in harmony with the assigned structures. Two *tert*-butyl and also two trialkylsilyl groups of **4** are equivalent both in the ¹H- and ¹³C-NMR spectra, showing that the sp²(C)-CMe₃ and sp²(C)-SiR₃ bonds are freely rotating at room temperature. This is probably due to the highly distorted structures of **4** which made the energy gap between the ground state and the transition state of the rotation smaller.⁵ Interestingly, in the ¹³C NMR spectra of **4**, the α-carbon signals of thiophene ring undergo an up-field shift with increase of steric congestion; δ 139.2 for **4a**, 135.7 for **4b** and 133.5 for **4c**, whereas the β-carbon signals remain nearly constant; δ 159.2 for **4a** and 160.3 for **4b** and **4c**.

An X-Ray crystal structure analysis of **4c** was carried out at -120 °C (Figures 1-3).⁶ The torsion angles C₅-C₂-C₃-C₆ and C₁-C₂-C₃-C₄ that amount to about 39° and 14°, respectively, make the thiophene ring no longer planar. The torsion angles Si₁-C₁-C₂-C₃ and Si₂-C₄-C₃-C₂ are about 27° and 32°, respectively. The C₂-C₃ bond (1.48 Å) is much longer than that of the parent thiophene (1.42 Å).⁷ The C₁-C₂ (1.39 Å) and C₃-C₄ (1.41 Å) bonds are also longer than that of the parent thiophene (1.37 Å).⁷ The C₅-C₂-C₃ and C₆-C₃-C₄ bond angles (126°) are comparable with those of the parent thiophene (125°).⁷ The C₁-C₂-C₅ and C₄-C₃-C₆ bond angles (120°) are smaller than those of the parent thiophene (124°), but instead Si₁-C₁-C₂ and Si₂-C₄-C₃ bond angles (142°) are far larger than those of the parent thiophene (128°), thus driving the triisopropylsilyl groups to the sterically open sulfur atom side and making S-C₁-Si₁ and S-C₄-Si₂ bond angles (110° and 109°) much smaller than those of the parent thiophene (120°). The above data reveal that **4c** is released from steric congestion mainly by expansion of bond angles (particularly Si₁-C₁-C₂ and Si₂-C₄-C₃ bond angles) and also by large torsion angles.

Figure 1. Crystal structure of the thiophene (**4c**).

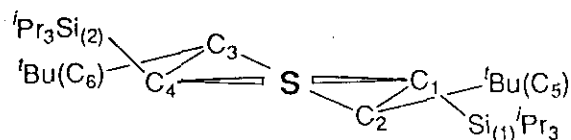
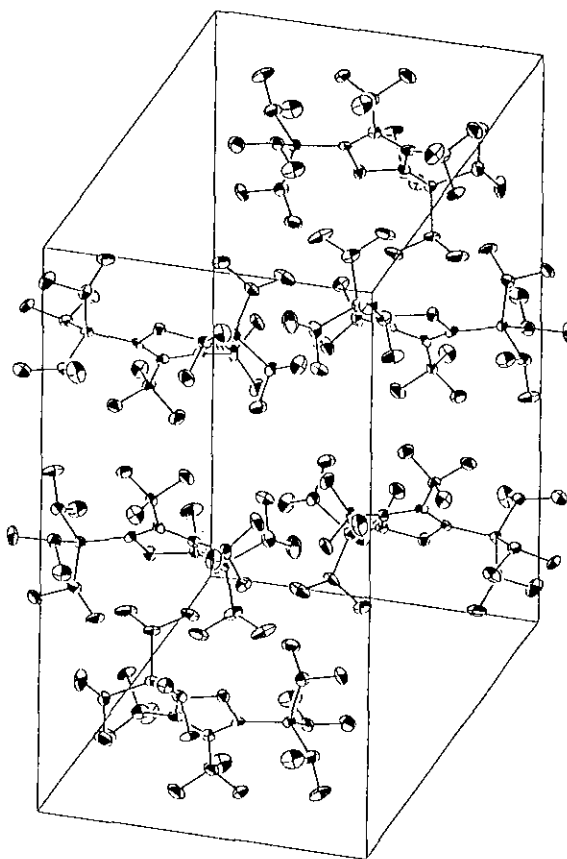


Figure 2. A side view of **4c** showing the nonplanar structure. Torsion angles ($^{\circ}$); Si(1)-C(1)-C(2)-C(5), 25.5; Si(2)-C(4)-C(3)-C(6), 32.4; C(5)-C(2)-C(4)-C(6), 38.8; C(1)-C(2)-C(3)-C(4), 14.1; S-C(1)-C(2)-C(3), 9.7; S-C(4)-C(3)-C(2), 11.4 (mean values of the three molecules).

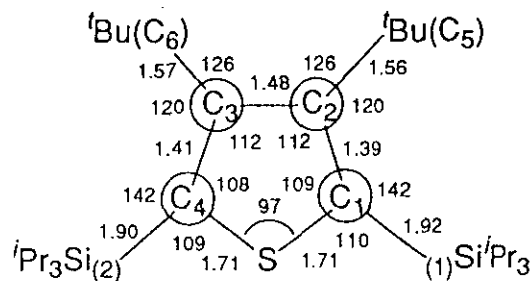


Figure 3. Selected bond lengths (\AA) and angles ($^{\circ}$) of **4c** (mean values of the three molecules).

All available data considered, the extent of the distortion of the molecular structure of **4c** from the parent thiophene seems to be comparable with that of tetra-*tert*-butylthiophene^{2,8} in spite of C-Si bonds being much longer than the corresponding C-C bonds.⁹

ACKNOWLEDGMENTS

The present work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (No. 09440213).

REFERENCES

1. a) J. Nakayama, S. Yamaoka, and M. Hoshino, *Tetrahedron Lett.*, 1988, **29**, 1161; b) J. Nakayama, S. Yamaoka, T. Nakanishi, and M. Hoshino, *J. Am. Chem. Soc.*, 1988, **110**, 6598; c) J. Nakayama and A. Hirashima, *J. Am. Chem. Soc.*, 1990, **112**, 7648; d) J. Nakayama, K. S. Choi, A. Ishii, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1026; e) J. Nakayama and R. Hasemi, *J. Am. Chem. Soc.*, 1990, **112**, 5654; f) J. Nakayama and K. Yoshimura, *Tetrahedron Lett.*, 1994, **35**, 2709.
2. A. W. Krebs, E. Franken, M. Müller, H. Collberg, W. Cholcha, J. Wilken, J. Ohrenberg, R. Albrecht, and E. Weiss, *Tetrahedron Lett.*, 1992, **33**, 5947.
3. J. Nakayama, H. Machida, R. Saito, and M. Hoshino, *Tetrahedron Lett.*, 1985, **26**, 1983.
4. **4a**: mp 141-142 °C; ¹H-NMR (CDCl₃, 200 MHz) δ 0.43 (18H, s, Me₃Si), 1.57 (18H, s, Me₃C); ¹³C-NMR (CDCl₃, 100 MHz) δ 4.1 (Me₃Si), 35.5 (Me₃C), 37.4 (Me₃C), 139.2 (α-carbons of the thiophene ring), 160.4 (β-carbons); MS (EI) *m/z* 340 (M⁺), 325 (M⁺-Me). **4b**: mp 82.5-83 °C; ¹H-NMR (CDCl₃, 400 MHz) δ 0.88-1.13 (30H, m, CH₃ and CH₂ of Et₃Si), 1.53 (18H, s, Me₃C); ¹³C-NMR (CDCl₃, 100 MHz) δ 7.3 (CH₃CH₂), 7.9 (CH₃CH₂), 35.4 (Me₃C), 36.9 (Me₃C), 135.7 (α-carbons of the thiophene ring), 160.3 (β-carbons); MS (EI) *m/z* 424 (M⁺), 395 (M⁺-Et). **4c**: mp 81.5-82 °C; ¹H-NMR (CDCl₃, 400 MHz) δ 1.05 (36H, d, *J* = 7.4 Hz, Me₂CH), 1.40 (18H, s, Me₃C), 1.4-1.5 (m, 6H, Me₂CH); ¹³C-NMR (CDCl₃, 100 MHz) δ 14.9 (Me₂CH), 19.8 (Me₂CH), 35.7 (Me₃C), 37.1 (Me₃C), 133.5 (α-carbons of the thiophene ring), 160.3 (β-carbons); MS (EI) *m/z* 508 (M⁺), 465 (M⁺-CHMe₂).
5. M. Oki in *Topics in Stereochemistry*, Vol 14, John Wiley, New York, 1983, p. 1.
6. Crystal data for **4c**: C₃₀H₆₀SSi₂, FW = 509.04, triclinic, space group; *P*1, *a* = 12.394(1) Å, *b* = 17.670(2) Å, *c* = 23.858(2) Å, α = 96.557(5)°, β = 97.538(5)°, γ = 108.554(6)°, *V* = 4842.5(9) Å³, *Z* = 6, *D*_c = 1.047 Mg m⁻³. The structure was solved by a direct method using CRYSTAN. Full matrix least-squares refinement was done on three molecules and yielded the final R value of 0.083 (*R*_w = 0.101) for 10120 independent reflections [*I* > 3.00σ(*I*)] using Mac Science DIP3000 diffractometers. Although **4c** was crystallized from a variety of solvents, the resulting crystals are triclinic in every case containing six molecules in a unit cell. This made difficult to improve further the final R values because of a great number of parameters to be considered. In Figure 1, only one molecule of the three is shown. Torsion angles data given under Figure 2 are average values of the three molecules. For example, three pairs of Si₁-C₁-C₂-C₃ and Si₂-C₄-C₃-C₂ torsion angles are 22.2 and 30.1°, 30.7 and 30.9°, and 26.8 and 36.2°, respectively. The bond lengths and angles data given in Figures 3 and 4 are also average values, which are in the range of three times of standard deviations.
7. R. M. Kellogg in *Comprehensive Heterocyclic Chemistry*, Vol. 4, ed. by C. W. Bird and G. W. H. Cheeseman, Chapter 3.10, Pergamon, Oxford, 1984.
8. The thiophene ring of 3,4-di-*tert*-butyl- and 3,4-di-1-adamantylthiophene is nearly planar: G. Bokkers, A. J. M. Duisenberg, J. Kroon, and L. Brandsma, *Cryst. Struct. Chem.*, 1985, **10**, 361; F. Iwasaki and J. Nakayama, unpublished results, although two adamantyl groups of the latter thiophene is twisted with a torsion angle of about 13°.
9. The bond lengths of Me₃Si-sp² and sp hybridized carbon bonds are found in the range 1.81-1.85 Å; W. S. Sheldrick in *The Chemistry of Organic Silicon Compounds, Part 1*, ed. by S. Patai, John Wiley, Chichester, 1989, p. 227.