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

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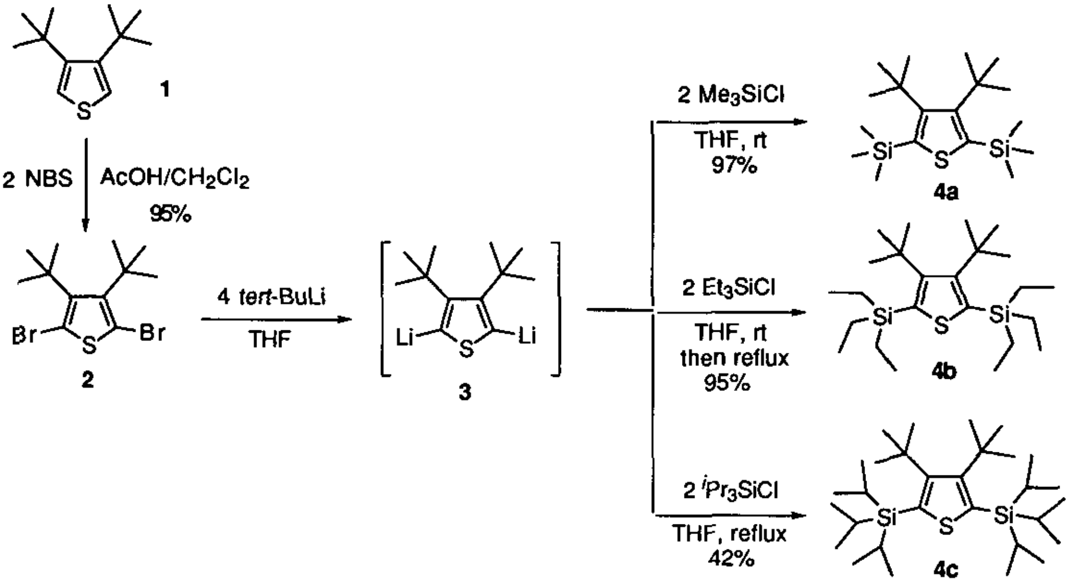
Abstract - Treatment of 2,5-dibromo-3,4-di-*tert*-butylthiophene with *tert*-butyllithium followed by reaction with triisopropylsilyl chloride gave a highly congested thiophene, 3,4-di-*tert*-buty-2,5-bis(triisopropylsilyl)thiophene, whose thiophene ring is no longer planar.

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 planed 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 alkyllithiums 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 data[4] 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 ^{1}H- and ^{13}C-NMR spectra, showing that the sp^2(C)-CMe$_3$ and sp^2(C)-SiR$_3$ 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 ^{13}C 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 C_5-C_2-C_3-C_6 and C_1-C_2-C_3-C_4 that amount to about 39° and 14°, respectively, make the thiophene ring no longer planar. The torsion angles Si_1-C_1-C_2-C_3 and Si_2-C_4-C_3-C_2 are about 27° and 32°, respectively. The C_2-C_3 bond (1.48 Å) is much longer than that of the parent thiophene (1.42 Å).[7] The C_1-C_2 (1.39 Å) and C_3-C_4 (1.41 Å) bonds are also longer than that of the parent thiophene (1.37 Å).[7] The C_5-C_2-C_3 and C_6-C_3-C_4 bond angles (126°) are comparable with those of the parent thiophene (125°).[7] The C_1-C_2-C_5 and C_4-C_3-C_6 bond angles (120°) are smaller than those of the parent thiophene (124°), but instead Si_1-C_1-C_2 and Si_2-C_4-C_3 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-C_1-Si_1 and S-C_4-Si_2 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 Si_1-C_1-C_2 and Si_2-C_4-C_3 bond angles) and also by large torsion angles.

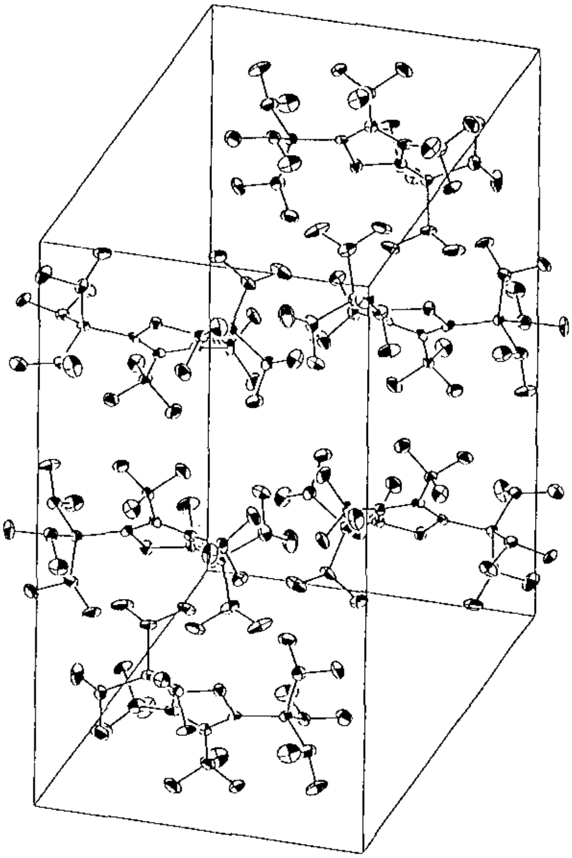


Figure 1. Crystal structure of the thiophene (**4c**).

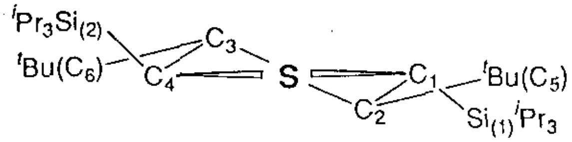


Figure 2. A side view of **4c** showing the nonplanar structure. Torsion angles (°); Si(1)-C(1)-C(2)-C(5), 25.5; Si(2)-C(4)-C(3)-C(6), 32.4; C(5)-C(2)-C(4)-C(6), 38.8; C(1)-C(2)-C(3)-C(4), 14.1; S-C(1)-C(2)-C(3), 9.7; S-C(4)-C(3)-C(2), 11.4 (mean values of the three molecules).

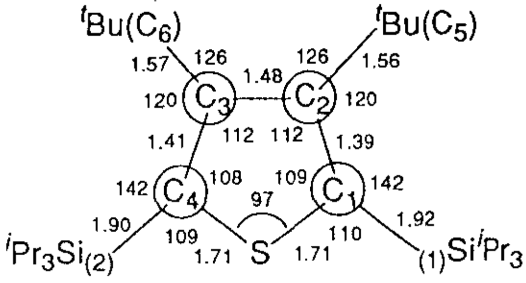


Figure 3. Selected bond lengths (Å) and angles (°) of **4c** (mean values of the three molecules).

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).

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4. **4a**: mp 141-142 °C; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.43 (18H, s, Me_3Si), 1.57 (18H, s, Me_3C); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 4.1 ($\underline{Me_3}Si$), 35.5 ($\underline{Me_3}C$), 37.4 ($Me_3\underline{C}$), 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; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.88-1.13 (30H, m, CH_3 and CH_2 of Et_3Si), 1.53 (18H, s, Me_3C); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 7.3 ($\underline{C}H_3CH_2$), 7.9 ($CH_3\underline{C}H_2$), 35.4 ($\underline{Me_3}C$), 36.9 ($Me_3\underline{C}$), 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; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.05 (36H, d, J = 7.4 Hz, $\underline{Me_2}CH$), 1.40 (18H, s, $\underline{Me_3}C$)), 1.4-1.5 (m, 6H, $Me_2\underline{CH}$); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 14.9 ($Me_2\underline{C}H$), 19.8 ($\underline{Me_2}CH$), 35.7 ($\underline{Me_3}C$), 37.1 ($Me_3\underline{C}$), 133.5 (α-carbons of the thiophene ring), 160.3 (β-carbons); MS (EI) *m/z* 508 (M^+), 465 (M^+–$CHMe_2$).

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6. Crystal data for **4c**: $C_{30}H_{60}SSi_2$, FW = 509.04, triclinic, space group; $P1$, 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) Å^3, Z = 6, Dc = 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 [$I > 3.00\sigma(I)$] using Mac Science DIP3000 difractometers. 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 Si_1-C_1-C_2-C_3 and Si_2-C_4-C_3-C_2 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 Me_3Si-sp^2 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.

Received, 9th May, 1997