Crystal and Molecular Structure of 5,5'-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl]-2,2'-bithiophene

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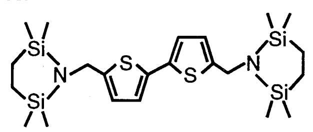
5,5'-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl]-2,2'-bithiophene crystallizes in the monoclinic system with space group $P2_1/c$. Because of the presence of the bulky terminal groups of 2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclo-pentyl, the compound shows unique crystallographic features compared with previously reported bithiophene and its derivatives.

The crystal structures of oligothiophenes[1,2] and polythiophenes[3,4] are currently under extensive investigation in connection with their unique electronic properties. Of these, the compounds having bulky or long side/end substituent groups show crystallographic features considerably different from those of the compounds without such substituent groups.[2,4] This motivated us to further study effects of the bulky groups upon the crystal structure.

In this article we report the crystal and molecular structure of 5,5'-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)-methyl]-2,2'-bithiophene[5] (**1**) that has extra bulky terminal groups. On account of these terminal groups of 2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl, the compound **1** shows peculiar crystallographic features among the family of bithiophenes.[6-8]



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Molecular structure and atomic numbering scheme of **1** are shown in Figure 1.[9] The coordinates of C6', S1', Si2' *etc.* are given by the inversion of the corresponding C6, S1, Si2 *etc.* relative to the molecular center (*i.e.* the center of the C6-C6' bond). The coplanarity encompassing the two backbone thiophene rings is strictly sustained and the deviation of the individual atoms on the rings from the least-squares plane defined by those atoms is at most 0.005 Å. This ring coplanarity is similarly characteristic of bithiophene and its derivatives.[6-8] The bond lengths and angles of the thiophene ring are well related as well to those of these bithiophenes.[6-8] The methylene carbons (C7 and C7') directly bonded to the thiophene rings are positioned very close to the bithiophene backbone plane.

Figure 2 shows a stereo view of the crystal packing of **1**. The overall crystallographic profile is characterized by two-dimensionally spreading molecular "sheets" that are stacked up along the *a* axis. The resulting molecular layered structure most frequently occurs in other bithiophene compounds such as 2,2'-bithiophene,[6] 5,5'-dimethyl-2,2'-bithiophene,[7] and 5,5'-bis(trimethylsilyl)-2,2'-bithiophene.[7] The space group $P2_1/c$ (or $P2_1/a$) is also noticed in common for these bithiophenes and for oligothiophenes having higher polymerization degrees more generally.[10]

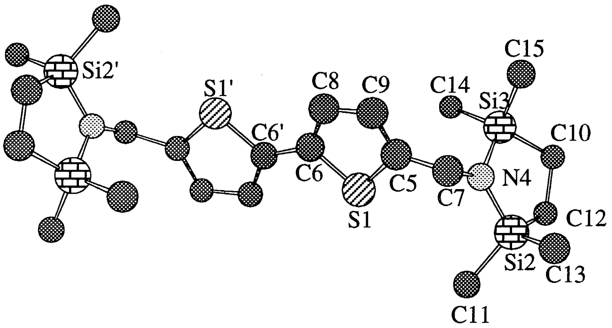

Figure 1. Molecular structure and atomic numbering of **1**. C6', S1', Si2', *etc.* are given by the inversion of the corresponding C6, S1, Si2, *etc.* relative to the molecule center. Selected bond distances (Å) and angles (°): S1-C5, 1.720(3); S1-C6, 1.728(3); Si2-N4, 1.720(2); Si2-C11, 1.857(5); Si2-C13, 1.845(6); Si2-C10, 1.859(5); N4-C7, 1.462(4); C5-C7, 1.494(5); C5-C9, 1.354(4); C6-C8, 1.364(4); C8-C9, 1.405(5); C10-C12, 1.523(8); C6-C6', 1.450(6); C5-S1-C6, 92.7(1); N4-Si2-C11, 110.9(2); N4-Si2-C10, 99.0(2); C13-Si2-C11, 108.2(3); C13-Si2-C10, 112.4(3); C11-Si2-C10, 114.2(2); C7-N4-Si2, 121.8(2); Si2-N4-Si3, 114.2(1); C9-C5-C7, 127.8(3); C9-C5-S1, 110.6(2); C7-C5-S1, 121.6(2); C8-C6-S1, 109.4(2); N4-C7-C5, 114.3(2); C6-C8-C9, 114.1(3); C5-C9-C8, 113.2(3); C12-C10-Si2, 109.0(4); S1-C6-C6', 129.5(4); C8-C6-C6', 121.1(3).

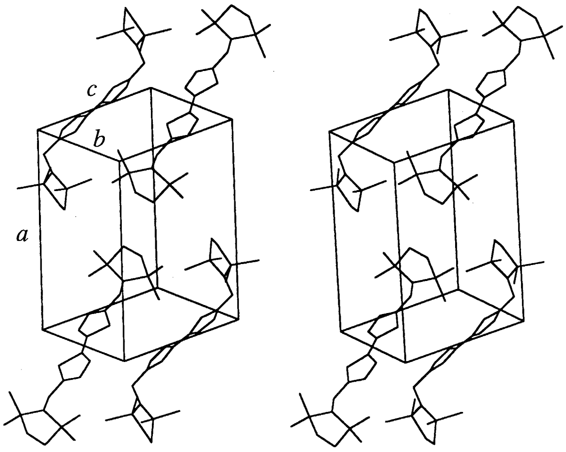

Figure 2. Stereo view of the crystal packing of **1**.

The molecular long axis (a line linking the methylene carbons bonded to the thiophene rings) meets with the *a* axis at an angle of 51.0°. The shortest atomic contact along the *a* axis is 3.96(1) Å for C10···C15, whereas that between the molecules within the *bc* plane is 3.698(6) Å for C8···C11. This indicates that the interaction between the molecules along the *a* axis is weaker than that along the *b* and *c* axes.

The bulky groups located at both the molecular terminals play a definitive role in the molecular packing in the crystal (Figure 2). These bulky terminal groups are largely bent relative to the bithiophene backbone, with its least-squares plane and that of the five-membered ring in the terminal group crossing at an angle 102.1°. The molecules glide over one another so as to be released from steric hindrance between the bulky terminal groups. As a result, in an adjacent pair of molecules the thiophene rings turn aside each other. This probably leads to weak π–π interaction between the molecules.

This feature is apparently related to that for 5,5'-bis(trimethylsilyl)-2,2'-bithiophene[7] which has relatively large groups of trimethylsilyl at both the molecular terminals. Nonetheless, essentially different aspects exist between that compound and **1**. The dihedral angle between the backbone least-squares planes for the adjacent pair of molecules for **1** is 24.0°, whereas that of 5,5'-bis(trimethylsilyl)-2,2'-bithiophene is 65.3°. The latter value is consistent with the corresponding angles of 35-68° observed or calculated for crystals having a normal herringbone structure.[6–8,11] This indicates that the herringbone structure does not persist in **1**, whereas that structure is retained in 5,5'-bis(trimethylsilyl)-2,2'-bithiophene. The difference is very likely attributed to that in size between the terminal groups of **1** and 5,5'-bis(trimethylsilyl)-2,2'-bithiophene. Notice that the groups of 2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl are even larger than the trimethylsilyl groups.

In summary, the crystals of the compound **1** in the present studies belong to the monoclinic system with space group $P2_1/c$ that is widely observed for the bithiophene compounds and are characterized by the molecular layered structure. The presence of the extra bulky terminal groups of **1** makes the thiophene rings in the adjacent pair of molecules turn aside and results in the absence of the normal herringbone structure.

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9 Crystal data for **1**: $C_{22}H_{40}N_2S_2Si_4$, M=511.20, monoclinic, space group $P2_1/c$, a=13.944(2), b=12.064(2), c=9.079(2) Å, β=101.21(2)°, Z=2, V=1503.5(5) Å^3, D_c=1.13 g/cm^3, λ(Cu $K\alpha$)=1.54178 Å. The apparatus was a Mac Science MXC18 four-circle diffractometer. Measurement was carried out at room temperature under ambient environment. No corrections were made for the absorption. Data analysis was carried out with the CRYSTAN program. The structure was solved by the direct method on a MULTAN and refined by the full-matrix least-squares method using 2503 reflections [$I>3\sigma(I)$] and 197 variable parameters with $R(R_w)$=0.073(0.107). All the non-hydrogen atoms were refined anisotropically.

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