

Crystal Structure of Tetrakis(2,2'-bithiophene-5-yl)silane

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The crystal structure of tetrakis(2,2'-bithiophene-5-yl)silane, $C_{16}H_{10}S_4Si_{0.5}$, has been determined at 293K in the Monoclinic (I2) symmetry. The Si atom has quasi-perfect tetrahedral geometry and bithiophene unit are quasi-planar. Comparison of Si-C bond lengths with literature data indicates an electron donating effect of the terminal thienyl ring on the first C linked to the Si central atom. The study of C-C bond lengths reveals a much more aromatic character for the four thienyl rings directly linked to the Si atom. The molecular packing arrangement shows that each molecule presents eight intermolecular contacts.

Keywords: crystal structure; tetrahedral; bithiophene; silane

In recent years, tetrahedral thiophene derivatives have been the focus of attention in organic electronics, particularly to solve low solubility problems of π -conjugated systems [1]. Several silanes tetrasubstituted by oligothiophenes having a supposed tetrahedral symmetry have been described as 3D electro-active π -conjugated material [2] as donor materials for organic solar cells [3,4]. In another field, conducting polymers have been largely studied to develop chemical sensors [5]. Thereby, they have been investigated to prepare molecularly imprinted polymers [6-8] acting both as recognition and transducing phase for electrochemical detection of molecular targets [9]. In order to improve and stabilize the imprinting effect, one of the challenges is to prepare imprinted conducting polymers with a tetrahedral cross-linker [10, 11]. In our ongoing research on surface plasmon resonance sensors [12], we develop an imprinted conducting polymer with

tetrakis(2,2'-bithiophene)silane (fig. 1) as cross-linker to maintain the 3D network of the sensing phase. In order to confirm its tetrahedral geometry we have resumed its synthesis [13] and determined its crystal structure.

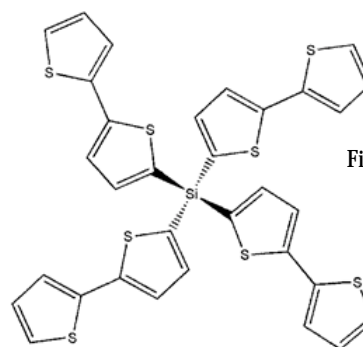


Fig.1. Structure of tetrakis(2,2'-bithiophene)silane

Table 1

CRYSTAL DATA, DATA COLLECTION AND STRUCTURE REFINEMENT. CAMBRIDGE CRYSTALLOGRAPHIC DATA CENTRE NUMBER: CCDC 1846056. COMPUTER PROGRAMS: CRYSTALIS PRO 1.171.38.43 (RIGAKU OD, 2015), SHELXS (SHELDRICK, 2008), SHELXL (SHELDRICK, 2015), OLEX2 (DOLOMANOV ET AL., 2009)

Crystal data	
Chemical formula	$C_{16}H_{10}S_4Si_{0.5}$
Mr	344.52
Crystal system, space group	Monoclinic, I2
Temperature (K)	293
a, b, c (Å)	13.6388 (6), 8.1961 (3), 14.6700 (6)
β (°)	97.594 (4)
V (Å ³)	1625.49 (11)
Z	4
Radiation type	Mo K α
μ (mm ⁻¹)	0.61
Crystal size (mm)	0.24 × 0.16 × 0.1

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Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, AtlasS2
Absorption correction	Multi-scan CrysAlis PRO 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
Tmin, Tmax	0.866, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5237, 3166, 2878
Rint	0.017
($\sin \theta/\lambda$) _{max} (\AA^{-1})	0.657
Structure Refinement	
R[F ² > 2 σ (F ²)], wR(F ²), S	0.048, 0.144, 1.09
No. of reflections	3166
No. of parameters	186
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	0.47, -0.33
Absolute structure	Flack x determined using 1186 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.08 (4)

Experimental part

Tetrakis(2,2'-bithiophene-5-yl)silane was synthesized in one-step reaction from commercial bithiophene. A solution of 2.0 g (0.012 mol) of 2,2'-bithiophene in 35 mL of anhydrous diethylether was placed under argon atmosphere and cooled at -40°C before addition of 6.0 mL (0.015 mol) n-BuLi (2.5 M in hexane). After one hour, 1.8 mL (0.012 mol) of tetramethoxysilane was added and the temperature increased to -20°C. After 2 h at -20°C, the mixture was diluted with dichloromethane and washed with water and introduced in a funnel for extraction. The aqueous phase was removed. The organic phase was dried with magnesium sulphate and filtrated. Finally, the solvents were evaporated using a rotary evaporator. Purification was performed on silica gel column with a mixture of cyclohexane/ethyl acetate (80/20) as eluent. The target compound was finally crystallized to give colourless single-crystal for X-ray diffraction analysis (details are summarized in table 1) and ¹H NMR. The compound analysis was carried out using a BrukerAvance 300 NMR and MestReNova software. MP: 154-155°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): δ 7.49 (d, ³J=3.6Hz, 4H), 7.37 (d, ³J=3.6Hz, 4H), 7.28 (dd, ³J=3.6Hz, ⁵J=1.2Hz, 4H), 7.26 (dd, ³J=3.6Hz, ⁵J=1.2Hz, 4H), 7.05 (dd, ³J=3.6 Hz, ³J=3.6Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 124, 124.5, 125.5, 128, 132, 137, 139.5, 145.5.

Result and discussions

The compound presented in ORTEP drawing in figure 2 crystallizes in the monoclinic space group I2. The crystal structure of tetrakis(2,2'-bithiophene-5-yl)silane is obtained from two half molecules in the asymmetric unit with an angle of 110.32° between C1-Si-C9 atoms. The coordination sphere around the Si atom is quasi-perfectly tetrahedral with angles from 108.71° for C1-Si-C1 angle to 110.33° for C1-Si-C9. The Si-C bond lengths of 1.848 Å (Si-C9) and 1.854 Å (Si-C1) are a little shorter than those in tetrakis(2-

thienyl)-silane (1.865(5) and 1.890(5) Å) [14] and identical to bond length found for tetrakis(3,4-ethylenedioxy-2-thienyl)-silane [1.848(2)Å] [15] which indicate an electron donating effect of the thienyl ring on the first one linked to Si atom. The average C-S bonds [1.716 (5) Å] of thienyl ring linked to Si atom are similar to those of tetrakis(2-thienyl)-silane with 1.714 Å [14] or thienyl rings in bithiophene [16] and in α -terthienyl [17]. C=C bond lengths in the thienyl ring linked to Si atom [C1-C2: 1.346(9) Å; C3-C4: 1.370(9) Å and C9-C10: 1.369(7) Å; C11-12: 1.38(8) Å] are similar to those of α -terthienyl i.e. shorter than C2-C3: 1.40(1) Å and C10-C11: 1.41(1) Å.

As far as the second thienyl ring of tetrakis(2,2'-bithiophene-5-yl)silane is concerned, the average C-S bonds [1.684(5)Å] are shorter than for the thienyl ring directly linked to Si. Furthermore, C5-C6 [1.483(8) Å] and C13-C14 [1.496(8) Å] are longer than C6-C7 [1.45(1) Å] and C14-C15 [1.47(1) Å], which indicates for these successive bonds a Csp²-Csp² single bond distance [1.48 Å]. From these observations, the thienyl ring linked to Si atom seems to be more aromatic than the second thienyl ring. This is confirmed by the difference between average Csp²-Csp² bond lengths of thienyl ring linked to Si atom (1.37 Å) to the end thienyl (1.42Å). Angles of 11.50 and 14.72° between thienyl rings are measured on asymmetric unit whereas the thienyl rings are coplanar in bithiophene or α -terthienyl. So these twist angles could explain the different aromatic character of the two thienyl rings in tetrakis(2,2'-bithiophene-5-yl)silane.

In the asymmetric unit, for one bithiophene each thienyl ring has one contact with two other molecules (fig 2).

For the other bithiophene, only the end thienyl ring has two contacts with two other molecules. In fact, the H and S atoms of end thienyl ring have intermolecular contacts with the C atom of the thienyl ring linked to Si atom of one molecule [C-H 2.871 Å] and H atom of thienyl ring of other one molecule [S-H 2.888Å]. Finally, each molecule has

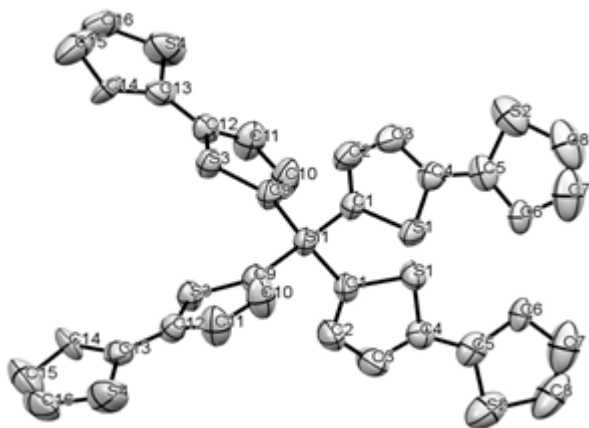


Fig. 2. The structure of tetrakis(2,2'-bithiophene-5-yl)silane showing 25% probability displacement ellipsoids and the atomic numbering scheme. H atoms have been omitted for clarity

eight intermolecular contacts with six other molecules because two C-H intermolecular contacts are made between two molecules (fig 3).

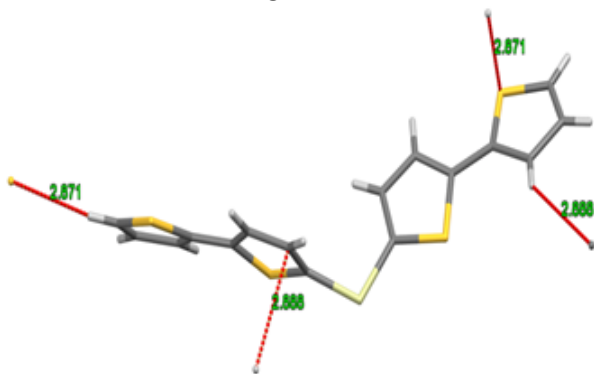


Fig. 3. Asymmetric unit of tetrakis(2,2'-bithiophene-5-yl)silane with intermolecular contacts

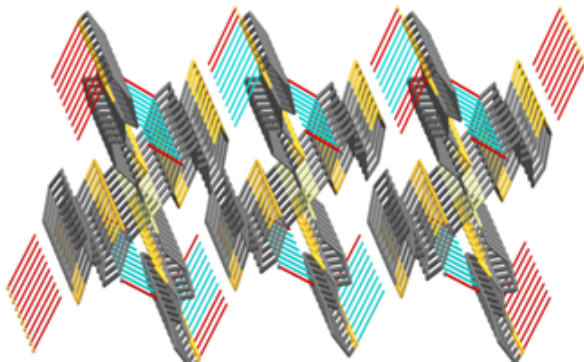


Fig. 4. Asymmetric unit of tetrakis(2,2'-bithiophene-5-yl)silane with short contacts

Conclusions

In conclusion, tetrakis(2,2'-bithiophene-5-yl)silane was synthesized to confirm its tetrahedral geometry. The compound gave colourless crystal in cyclohexane. Single-

crystal X-ray diffraction has shown a monoclinic symmetry, eight intramolecular interaction between the bithiophenyl moieties and as expected a tetrahedral silicon. A significant difference of structure was observed between the two thienyl rings of the bithiophenyl substituents which were ascribed to partial loss of aromaticity of the ring farthest from the central Si.

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