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Tetrakis(3,4-ethylenedioxy-2-thienyl)silane carbon tetrachloride solvate

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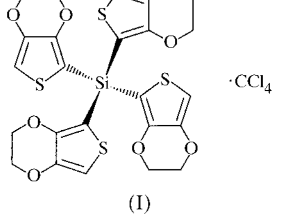
The structure of tetrakis(3,4-ethylenedioxy-2-thienyl)silane carbon tetrachloride solvate, $Si(C_6H_5O_2S)_4 \cdot CCl_4$, has been determined in the non-centrosymmetric space group $I\bar{4}$. The Si and C atoms of the CCl_4 are located on the fourfold inversion axes. The Si atom has a tetrahedral geometry. The thiophene ring in the 3,4-ethylenedioxythiophene group is planar to within 0.005 Å and the ethylenedioxy moiety is in a half-chair conformation.

Comment

Thiophene derivatives have attracted attention in the field of materials chemistry due to their ease of derivatization and their ability to be polymerized using a variety of chemical and electrochemical methods (Roncali, 1997; Jestin *et al.*, 1998; Visy *et al.*, 1996). Polythiophene derivatives show interesting electronic, optical and electrochemical properties. One of the most interesting polythiophene derivatives is poly(3,4-ethylenedioxythiophene) (PEDOT), because it has a much lower bandgap, better environmental stability and higher conductivity than polythiophene (Sotzing *et al.*, 1997). Recently, PEDOT has been utilized in the field of electrochromics because of its highly transmissive oxidized state, opaque deep-blue reduced state and high contrast ratio (Kumar *et al.*, 1998; Sankaran & Reynolds, 1997). In the course of our ongoing research on electrochromic materials, we have synthesized tetrakis(3,4-ethylenedioxy-2-thienyl)silane carbon tetrachloride solvate, (I), as a novel precursor for poly(3,4-ethylenedioxythiophene) and have determined its crystal structure.



(I)

An *ORTEP* drawing of (I) is presented in Fig. 1. The compound cocrystallizes with CCl_4 in a 1:1 ratio in the non-centrosymmetric space group $I\bar{4}$. Since Z is 2, the Si atoms reside on the $\bar{4}$ axes at $(0,\frac{1}{2},\frac{1}{4})$ and $(0,\frac{1}{2},\frac{3}{4})$, as shown in Fig. 2. The asymmetric unit consists of a quarter of an Si atom, one ethylenedioxythienyl ring and a quarter of a CCl_4 molecule. The C atoms of the CCl_4 solvate occupy fourfold inversion axes at the special positions (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the Cl atoms are in general positions, as shown in Fig. 2.

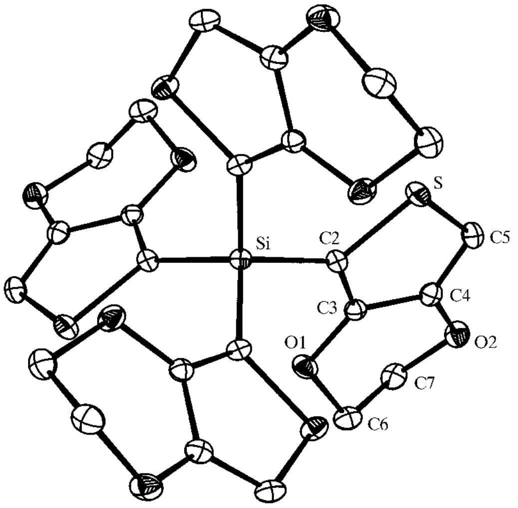


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids and the atomic numbering scheme. The carbon tetrachloride molecule and the H atoms have been omitted for clarity.

The coordination sphere around the Si atom is perfectly tetrahedral due to the symmetry definition. The Si atom lies in the thienyl ring plane and each thienyl ring is planar to within an average standard deviation from planarity of the thienyl atoms of 0.005 Å. The Si—C bond length of 1.848 (2) Å is very

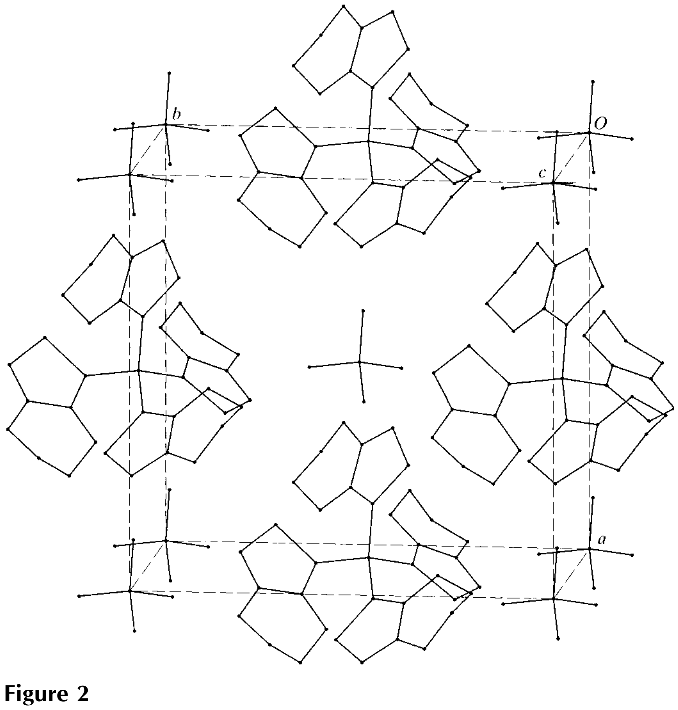


Figure 2
The molecular packing diagram for (I).

close to that found in phenylsilane [1.843 (5) Å; Keidel & Bauer, 1956], but shorter than those in tetrakis(2-thienyl)silane and tetraphenylsilane [1.888 (3) and 1.872 (7) Å, respectively; Glidewell & Sheldrick, 1971]. The average C—S distance [1.727 (6) Å] in the thienyl ring is very similar to the mean C—S distances in 1,2-bis[2-(3,4-ethylenedioxy)thienyl]vinylene and 1,4-bis[2-(3,4-ethylenedioxy)thienyl]benzene [1.725 (3) and 1.728 (2) Å, respectively; Sotzing *et al.*, 1996]. The C—C bond lengths in the thienyl ring are very similar to those of the corresponding C—C bond distances in free thiophene (Bak *et al.*, 1961; Harshbarger & Bauer, 1970). The C3—C4 bond length [1.426 (3) Å] in the thienyl ring is significantly longer than those of C2—C3 [1.364 (3) Å] and C4—C5 [1.354 (3) Å]; however, all three C—C bond lengths differ from normal Csp^2—Csp^2 single [1.48 Å] and Csp^2═Csp^2 double [1.34 Å] bond distances. The average C—S bond distance [1.727 (6) Å] is somewhat shorter than a normal Csp^2—S single-bond length [1.759 (8) Å], but is longer than the corresponding C—S distance of free thiophene [1.714 (1) Å; Angelici, 1990]. Therefore, the thienyl ring structure indicates some delocalization of the π-electrons, but less than is found in free thiophene. The C2—S—C5 angle [93.4 (1) Å] is the same, to within experimental error, as those in free thiophene, in 3,4-ethylenedioxythiophyene derivatives (Sotzing *et al.*, 1996) and in S-bound thiophene transition metal complexes (Angelici, 1990; Choi & Angelici, 1991).

The six-membered dioxane ring is in a half-chair conformation. The structural features of the dioxane moiety in (I) are close to those found in 2-(1,2-dibromoethyl)-1,4-benzodioxan (Barnes & Schroth, 1988) and bis(1,4-benzodioxan)silver(I) perchlorate (Barnes & Blyth, 1985). The angle between the thienyl ring and the C6—C7 bond is 30.4 (2)°. The H atoms on the ethylene C atoms have a nearly *gauche* configuration.

Experimental

To freshly distilled diethyl ether (30 ml) in a Schlenk flask was added 3,4-ethylenedioxythiophene (1.0 g, 7.0 mmol) under an Ar atmosphere. The solution was cooled to 195 K with a dry ice–acetone bath and *n*-butyllithium (4.4 ml, 1.6 *M* in *n*-hexane) was added slowly over 15 min using a dropping funnel. The dry ice–acetone bath was then replaced with an ice bath. After 30 min, the ice bath was removed and the resulting light-yellow solution, containing the white salt, was stirred at room temperature for 2 h. Next, tetrachlorosilane (0.2 ml, 1.7 mmol) was dissolved in distilled diethyl ether (15 ml) in another Schlenk flask in an ice bath and added slowly *via* a cannula. After 10 min, the ice bath was removed and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was then added to CH_2Cl_2 (100 ml), and washed with water (30 ml) and brine (30 ml) twice. The organic phase was dried over $MgSO_4$, filtered and evaporated to give a light-brown liquid. The crude product was purified by column chromatography (2 × 15 cm, silica gel, CH_2Cl_2 eluent). Evaporation of the eluent under vacuum gave a white solid. This was recrystallized from a saturated CH_2Cl_2 solution by a slow cooling method to give colourless transparent crystals of (I) (0.32 g, 0.54 mmol, 31% yield). Crystals suitable for X-ray crystallography were obtained by very slow cooling using a double Dewar technique in a saturated CCl_4 solution. ^{1}H NMR (δ, acetone-d_6/DMSO-d_6, p.p.m.): 6.7 (*s*, 4H), 4.1 (*m*, 16H); analysis calculated for $C_{24}H_{20}O_8S_4Si$: C 48.63, H 3.40%; found: C 48.48, H 3.56%.

Crystal data

$C_{24}H_{20}O_8S_4Si\cdot CCl_4$
$M_r = 746.54$
Tetragonal, $I\bar{4}$
$a = 13.1846$ (6) Å
$c = 8.8493$ (6) Å
$V = 1538.31$ (14) Å^3
$Z = 2$
$D_x = 1.612$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3266 reflections
$\theta = 4$–$53°$
$\mu = 0.742$ mm^{-1}
$T = 193$ (2) K
Block, colourless
0.41 × 0.18 × 0.18 mm

Data collection

Siemens CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.751$, $T_{\max} = 0.878$
1557 measured reflections

836 independent reflections (plus 721 Friedel-related reflections)
1480 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 26.35°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.005$
1557 reflections
115 parameters
Only H-atom U's refined

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.401P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.08 (8)

Table 1
Selected geometric parameters (Å, °).

Si—C2	1.848 (2)	O1—C6	1.441 (3)
S—C2	1.734 (2)	O2—C4	1.380 (3)
S—C5	1.721 (3)	O2—C7	1.447 (3)
O1—C3	1.372 (3)		
C2—S—C5	93.42 (11)	O2—C4—C3	123.1 (2)
C3—C2—S	108.83 (16)	C4—C5—S	110.51 (17)
C3—C2—Si	129.22 (17)	O1—C6—C7	110.54 (19)
S—C2—Si	121.95 (12)	O2—C7—C6	110.4 (2)
C2—C3—O1	123.3 (2)	C3—O1—C6	111.37 (18)
O1—C3—C4	122.3 (2)	C4—O2—C7	111.08 (18)
C5—C4—O2	124.0 (2)		
C2—C3—O1—C6	163.8 (2)	C4—O2—C7—C6	46.2 (3)
O1—C6—C7—O2	−65.4 (3)	C6—O1—C3—C4	−17.2 (3)

H atoms were located from a difference electron-density map and refined using isotropic displacement parameters; C—H distances are in the range 0.91 (4)–0.99 (3) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure program(s) used to refine structure; molecular graphics; and software used to prepare material for publication: *SHELXTL* (Siemens, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1098). Services for accessing these data are described at the back of the journal.

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