ods in *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octabutyltetrasila[2.2]terthiophenophane

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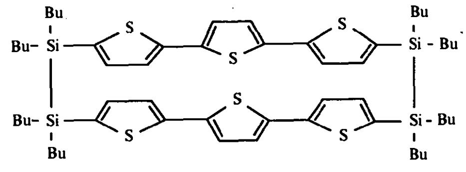
Abstract

The title compound, 1,1,1′,1′,2,2,2′,2′-octabutyl-1,1′,2,2′-tetrasila[2.2](9,20)α,α'-terthiophenophane (10,10,11,11,24,24,25,25-octa-*n*-butyl-29,30,31,32,33,34-hexathia-10,11,24,25-tetrasilaheptacyclo[24.2.1.$1^{2,5}$.$1^{6,9}$.$1^{12,15}$.$1^{16,19}$.$1^{20,23}$]tetratriaconta-2,4,6,8,12,14,16,18,20,22,26,28-dodecaene, $C_{56}H_{84}S_6Si_4$) provides the first example of the crystal structure of a [2.2]thiophenophane bridged by silanes. The molecule is centrosymmetric and the thiophene rings are nearly planar.

Comment

As part of our studies of the synthesis and structures of poly(silanylene)thiophenes, we recently reported the isolation of cyclic compounds formed as by-products during the synthesis of the polymers (Wildeman, Herrema, Hadziioannou & Schomaker, 1991). These cyclic compounds, consisting of σ–π conjugations, are of interest because of their special electronic and chemical properties. A few X-ray data on paracyclophanes are given in the literature and, although the photoelectron spectrum of octamethyltetrasila[2.2](2,5)thiophenophane has been reported (Gleiter, Schäfer, Krennrich & Sakurai, 1988), no crystal structure of a thiophenophane bridged by polysilanes has been reported until now.



(I)

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The title compound (I) is a by-product of the synthesis of a polymer which we are studying as the active layer in light-emitting diodes (Herrema *et al.*, 1993). The triclinic unit cell contains only one molecule; this molecule has a centre of symmetry. The thiophene rings are virtually planar (to within 0.012 Å) and adjacent rings lie in an antiparallel orientation. The angles between the least-squares plane through the atoms S2, C13, C14, C15 and C16 (ring 2) and the planes through S1, C9, C10, C11 and C12 (ring 1) and S3, C17, C18, C19 and C20 (ring 3) are 8.1 (9) and 7.7 (9)°, respectively. These values compare well with the torsion angles of the thiophene rings of α-terthienyl (van Bolhuis, Wijnberg, Havinga, Meijer & Staring, 1989). The distance between the facing intramolecular thiophene rings 2 and 2′ is 3.607 Å, which is somewhat larger than the distance between the two aromatic rings in octamethyltetrasila[2.2]paracyclophane (3.4 Å) (Sakurai, Hoshi, Kamiya, Hosomi & Kabuto, 1986). The thiophene rings 2 and 2′ lie almost 'face-to-face' whereas in the other thiophene rings, 1 and 3, the S atoms lie above the middle of the opposite rings, resulting in a short S· · ·S distance (3.55 Å). These intramolecular S· · ·S distances are slightly smaller than twice the van der Waals radius of sulfur (1.85 Å), while the other intra- and intermolecular S· · ·S distances are all longer than the van der Waals contacts. The C—S bond lengths, which range from 1.723 (4) to 1.737 (5) Å with an average value of 1.730 Å, are close to the reported mean value of 1.712 Å (Allen *et al.*, 1987). The Si—Si bond length [2.363 (2) Å] is slightly longer than a normal Si—Si bond (2.34 Å). The conformation of the Si—Si bridges is intermediate between *gauche* and eclipsed, the torsion angle C9—Si1—Si2′—C20′ being 35.2°. The butyl groups have a planar zigzag conformation with the exception of the butyl group formed by C5, C6, C7 and C8.

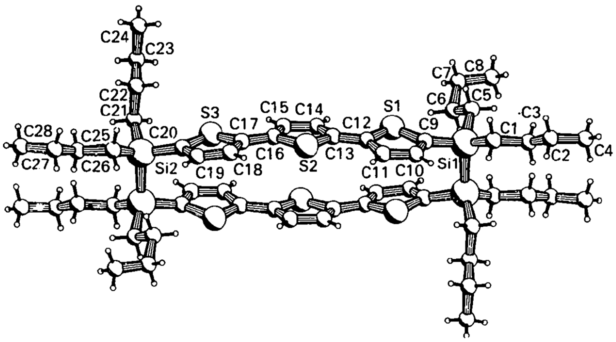

Fig. 1. *PLUTO* drawing of (I) illustrating the configuration and the atom-numbering scheme.

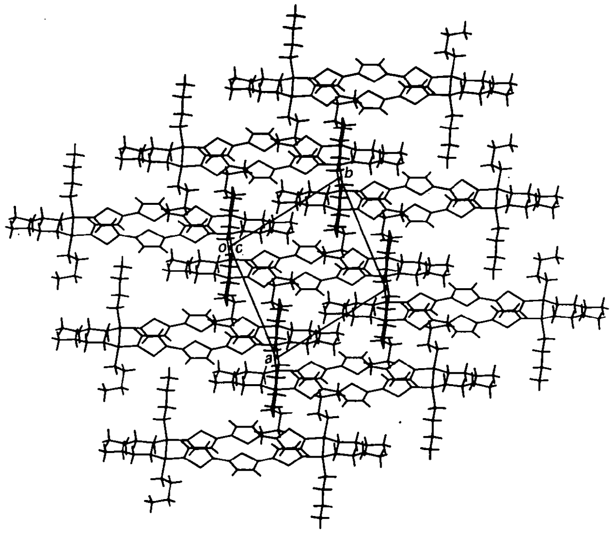

Fig. 2. Projected packing plot of the molecules in the unit cell and its surroundings viewed down the *c* axis.

Experimental

The title compound was synthesized by reacting dichlorotetrabutyldisilane with the dilithium salt of α-terthiophene in diethyl ether. After removal of the polymer by precipitation followed by chromatographic separation, compound (I) was recrystallized slowly from a mixture of dichloromethane and methanol.

Crystal data

$C_{56}H_{84}S_6Si_4$
$M_r = 1062.02$
Triclinic
$P\bar{1}$
$a = 10.468\ (2)$ Å
$b = 11.755\ (2)$ Å
$c = 12.862\ (1)$ Å
$\alpha = 106.96\ (1)°$
$\beta = 93.72\ (1)°$
$\gamma = 97.68\ (1)°$
$V = 1491.2\ (6)$ Å^3
$Z = 1$
$D_x = 1.183$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.7$-$18.6°$
$\mu = 0.332$ mm^{-1}
$T = 130$ K
Block
0.30 × 0.30 × 0.25 mm
Yellowish green

Data collection

Enraf-Nonius CAD-4F diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3669 measured reflections
3669 independent reflections
2570 observed reflections $[I > 3\sigma(I)]$

$\theta_{\max} = 22°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections frequency: 180 min intensity variation: 2.9%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.048$
$S = 1.49$
2570 reflections
298 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.39$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S1	0.4404 (1)	0.1225 (1)	0.4206 (1)	1.78 (3)
S2	0.5195 (1)	0.4646 (1)	0.68442 (9)	1.98 (3)
S3	0.8183 (1)	0.7628 (1)	0.68650 (9)	1.55 (2)
Si1	0.2207 (1)	−0.1051 (1)	0.3261 (1)	1.56 (3)
Si2	0.9075 (1)	1.0361 (1)	0.7938 (1)	1.42 (3)
C1	0.1244 (5)	−0.1965 (4)	0.4025 (4)	2.1 (1)
C2	0.0480 (6)	−0.3166 (5)	0.3340 (4)	3.1 (1)
C3	−0.0232 (5)	−0.3896 (4)	0.3993 (4)	2.7 (1)
C4	−0.0934 (6)	−0.5107 (5)	0.3280 (5)	4.7 (2)
C5	0.3443 (5)	−0.1905 (4)	0.2531 (4)	2.3 (1)
C6	0.4176 (5)	−0.1354 (4)	0.1758 (4)	2.5 (1)
C7	0.5215 (5)	−0.2054 (5)	0.1236 (5)	3.4 (1)
C8	0.4703 (6)	−0.3295 (5)	0.0515 (5)	4.9 (2)
C9	0.2979 (4)	0.0366 (4)	0.4341 (3)	1.6 (1)
C10	0.2476 (5)	0.0990 (4)	0.5243 (4)	2.0 (1)
C11	0.3182 (5)	0.2135 (4)	0.5820 (4)	2.0 (1)
C12	0.4273 (4)	0.2404 (4)	0.5342 (4)	1.8 (1)
C13	0.5212 (4)	0.3501 (4)	0.5648 (4)	1.7 (1)
C14	0.6193 (5)	0.3809 (4)	0.5082 (4)	2.2 (1)
C15	0.6912 (5)	0.4959 (4)	0.5603 (4)	2.1 (1)
C16	0.6493 (4)	0.5549 (4)	0.6563 (4)	1.45 (9)
C17	0.6950 (4)	0.6748 (4)	0.7254 (4)	1.6 (1)
C18	0.6547 (4)	0.7412 (4)	0.8196 (4)	1.7 (1)
C19	0.7194 (4)	0.8625 (4)	0.8578 (4)	1.5 (1)
C20	0.8120 (4)	0.8894 (4)	0.7941 (4)	1.5 (1)
C21	1.0617 (4)	0.9980 (4)	0.7338 (4)	1.6 (1)
C22	1.1445 (4)	0.9417 (4)	0.8013 (4)	2.1 (1)
C23	1.2556 (5)	0.8892 (5)	0.7421 (4)	2.7 (1)
C24	1.3380 (5)	0.8355 (5)	0.8116 (5)	3.7 (1)
C25	0.9441 (5)	1.1393 (4)	0.9366 (4)	1.9 (1)
C26	1.0342 (5)	1.2577 (4)	0.9465 (4)	2.5 (1)
C27	1.0609 (5)	1.3431 (5)	1.0606 (4)	2.6 (1)
C28	1.1611 (6)	1.4522 (5)	1.0674 (5)	3.4 (1)

Table 2. *Selected geometric parameters* (Å, °)

Si1—Si2	2.363 (2)	C7—C8	1.488 (7)
S1—C9	1.734 (5)	C9—C10	1.359 (6)
S1—C12	1.723 (4)	C10—C11	1.410 (6)
S2—C13	1.726 (4)	C11—C12	1.375 (7)
S2—C16	1.734 (5)	C12—C13	1.449 (6)
S3—C17	1.737 (5)	C13—C14	1.367 (7)
S3—C20	1.723 (4)	C14—C15	1.407 (6)
Si1—C1	1.894 (5)	C15—C16	1.360 (6)
Si1—C5	1.876 (5)	C16—C17	1.428 (5)
Si1—C9	1.872 (4)	C17—C18	1.363 (6)
Si2—C20	1.876 (5)	C18—C19	1.422 (6)
Si2—C21	1.886 (5)	C19—C20	1.373 (7)
Si2—C25	1.864 (4)	C21—C22	1.528 (7)
C1—C2	1.512 (6)	C22—C23	1.531 (7)
C2—C3	1.525 (8)	C23—C24	1.523 (9)
C3—C4	1.510 (7)	C25—C26	1.540 (7)
C5—C6	1.529 (8)	C26—C27	1.501 (6)
C6—C7	1.524 (8)	C27—C28	1.522 (7)
C9—S1—C12	93.5 (2)	C13—C14—C15	113.3 (4)
C13—S2—C16	92.6 (2)	C14—C15—C16	114.1 (4)
C17—S3—C20	93.8 (2)	S2—C16—C15	109.8 (3)
S1—C9—Si1	122.8 (2)	S2—C16—C17	121.8 (3)
S1—C9—C10	108.4 (3)	S3—C17—C16	118.9 (3)
C9—C10—C11	115.9 (4)	S3—C17—C18	109.4 (3)
C10—C11—C12	111.9 (4)	C17—C18—C19	113.6 (4)
S1—C12—C11	110.3 (3)	C18—C19—C20	113.9 (4)
S1—C12—C13	120.6 (4)	S3—C20—Si2	118.2 (3)
S2—C13—C12	121.9 (4)	S3—C20—C19	109.3 (3)
S2—C13—C14	110.2 (3)		
C1—C2—C3—C4	−177.6 (5)	S2—C16—C17—S3	−175.7 (3)
C5—C6—C7—C8	63.2 (6)	S2—C16—C17—C18	0.3 (7)
S1—C12—C13—S2	−174.2 (3)	C15—C16—C17—C18	176.9 (5)
S1—C12—C13—C14	6.6 (7)	C21—C22—C23—C24	179.1 (4)
C11—C12—C13—C14	−170.8 (5)	C25—C26—C27—C28	174.0 (4)

Data collection, cell refinement, data reduction, structure solution and structure refinement: *MolEN* (Fair, 1990). Molecular graphics: *PLUTO* (Meetsma, 1991; Motherwell & Clegg, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1057). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Charge-Transfer Complexes. 3. 2,4,5,7-Tetranitro-9-fluorenone–2-Ethylnaphthalene (1/1)

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Abstract

The π–π^* charge-transfer complex, $C_{13}H_4N_4O_9.C_{12}H_{12}$, stacks along the c-glide direction with the pair

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