organic papers

2,5-Bis(trimethylsilylethynyl)thieno[3,2-b]thiophene

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Key indicators

Single-crystal X-ray study
$T = 170$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.100
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

2,5-Bis(trimethylsilylethynyl)thieno[3,2-b]thiophene, $C_{16}H_{20}S_2Si_2$, is a trimethylsilyl-protected diyne. It is a precursor in the formation of platinum and gold diyne complexes and and polyyne polymers. These materials are of interest because of the π-conjugation that extends through the fused oligothienyl linker unit along the rigid backbone of the polymer. In the structure of the title compound, the oligothienyl group is planar, by crystallographic symmetry, and the trimethylsilyl-alkyne groups are essentially linear.

Comment

We report here the structural characterization of the title compound, 2,5-bis(trimethylsilylethynyl)thieno[3,2-b]thio-phene, (I), which is a trimethylsilyl-protected diyne. It is a precursor in the formation of the following series of compounds: the terminal diyne, $H-C\equiv C-R-C\equiv C-H$, the dinuclear platinum(II) diyne, $[(Ph)(PEt_3)_2Pt-C\equiv C-R-C\equiv C-Pt(PEt_3)_2(Ph)]$, and the platinum(II) polyyne, $trans$-$[(^nBu_3P)_2Pt-C\equiv C-R-C\equiv C-]_\infty$ (R = thieno[3,2-b]thiophene-2,5-diyl). Rigid-rod platinum(II) polyynes with the general formula $trans$-$[(^nBu_3P)_2Pt-C\equiv C-R-C\equiv C-]_\infty$ (R = conjugated aromatic/hetero-aromatic linker group) are considered to be good model systems to study the triplet excited state in polymers and provide important information on the photophysical processes that occur within them (Khan, Al-Mandhary, Al-Suti, Hisham *et al.*, 2002; Khan, Al-Mandhary, Al-Suti, Feeder *et al.*, 2002; Khan *et al.*, 2003). The incorporation of heavy transition metals, such as platinum, at regular intervals along the rigid polymer back-bone introduces a large component of spin-orbit coupling that allows emission from the triplet excited state of the system *via* spin cross-over processes (Wittmann *et al.*, 1994; Beljonne *et al.*, 1996; Younus *et al.*, 1998; Chawdhury *et al.*, 1999). The novel photophysics of the platinum(II) polyynes leads to materials that are useful for applications in modern opto-electronic devices such as light emitting diodes (LEDs), lasers, photocells and field-effect transistors (FETs) (Wilson *et al.*, 2000; Wilson, Chawdhury *et al.*, 2001; Wilson, Dhoot *et al.*, 2001).

(I)
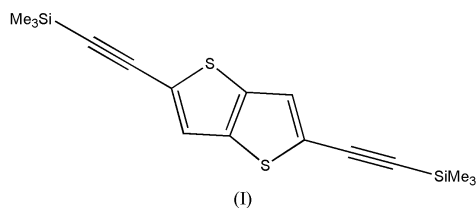
The title compound, (I), crystallizes in the monoclinic space group $P2_1/c$, with two molecules in the unit cell, such that each

molecule sits on a crystallographic centre of symmetry at the centre of the bithiophene unit, at the mid-point of the C8—C8a bond (Fig. 1), and the asymmetric unit contains half of one molecule. The bithiophene unit is planar. Within the bithiophene unit, the S—C bond lengths average 1.730 Å, and the C6—C7 and C8—C8a bond lengths (average 1.395 Å) are significantly shorter than the C7—C8 bond, 1.444 (3) Å, consistent with the normal bonding picture for bithiophene, and similar to those found in a binuclear platinum(II) complex bridged by a thieno[3,2-b]thiophene group (Sato *et al.*, 2002). The bond parameters associated with the acetylenic units and the trimethylsilyl groups are similar to those in a number of other bis(trimethylsilyl) substituted diyne compounds (Khan, Ahrens *et al.*, 2002, 2004).

There are no short intermolecular contacts within the crystal structure.

Experimental

To a solution of 2,5-dibromothieno[3,2-b]thiophene (2.0 g, 6.71 mmol) in ^{i}Pr$_2$NH–THF (70 ml, 1:1 *v/v*) under nitrogen was added a catalytic mixture of CuI (20 mg), Pd(OAc)$_2$ (20 mg) and PPh$_3$ (60 mg). The solution was stirred for 20 min at 323 K and then trimethylsilylethyne (1.64 g, 16.7 mmol) was added. The reaction mixture was left, with stirring, for 20 h at 348 K. The solution was allowed to cool down to room temperature, filtered and the solvent mixture removed under reduced pressure. The residue was subjected to silica column chromatography using hexane to afford the title compound as a colourless solid in 85% yield (1.78 g).

Crystal data

C$_{16}$H$_{20}$S$_2$Si$_2$	$D_x = 1.217$ Mg m^{-3}
$M_r = 332.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3713
$a = 15.173$ (3) Å	reflections
$b = 5.7317$ (12) Å	$\theta = 2.9$–25.0°
$c = 10.9836$ (18) Å	$\mu = 0.42$ mm^{-1}
$\beta = 108.220$ (9)°	$T = 170$ (2) K
$V = 907.3$ (3) Å^3	Needle, colourless
$Z = 2$	$0.23 \times 0.07 \times 0.04$ mm

Data collection

|	
Nonius KappaCCD diffractometer	$R_{int} = 0.022$
φ and ω scans	$\theta_{max} = 25.1°$
Absorption correction: none	$h = -17 \rightarrow 18$
2820 measured reflections	$k = -6 \rightarrow 6$
1596 independent reflections	$l = -13 \rightarrow 12$
1336 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 0.7998P]$
$wR(F^2) = 0.100$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1596 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
94 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H-atom parameters constrained	

All the aromatic and methyl H atoms were constrained as riding atoms, fixed to the parent atoms with distances of 0.95 and 0.98 Å, respectively, with $U_{iso}(H)$ set at 1.2 (aromatic H atoms) or 1.5 (methyl H atoms) times U_{eq}(parent atom).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL*
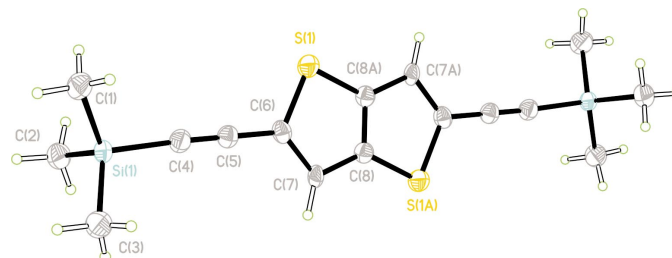
Figure 1
View of (I) (50% probability displacement ellipsoids). Atoms with the suffix *A* are the symmetry equivalents, related by $1 - x, -y, 1 - z$

DENZO and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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supporting information

2,5-Bis(trimethylsilylethynyl)thieno[3,2-*b*]thiophene

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(I)

Crystal data

$C_{16}H_{20}S_2Si_2$	$F(000) = 352$
$M_r = 332.62$	$D_x = 1.217$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.173$ (3) Å	Cell parameters from 3713 reflections
$b = 5.7317$ (12) Å	$\theta = 2.9–25.0°$
$c = 10.9836$ (18) Å	$\mu = 0.42$ mm^{-1}
$\beta = 108.220$ (9)°	$T = 170$ K
$V = 907.3$ (3) Å^3	Plate, colourless
$Z = 2$	$0.23 \times 0.07 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.022$
88 2° φ and 32 2° ω scans	$\theta_{max} = 25.1°$, $\theta_{min} = 3.8°$
2820 measured reflections	$h = -17 \rightarrow 18$
1596 independent reflections	$k = -6 \rightarrow 6$
1336 reflections with $I > 2\sigma(I)$	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.7998P]$
$wR(F^2) = 0.100$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1596 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
94 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.55976 (4)	−0.07228 (11)	0.35782 (6)	0.0324 (2)
Si1	0.82072 (4)	0.56440 (11)	0.30149 (6)	0.0245 (2)
C1	0.88762 (18)	0.3625 (5)	0.2313 (3)	0.0378 (6)

H1A	0.9153	0.2391	0.2932	0.057*
H1B	0.9368	0.4493	0.2108	0.057*
H1C	0.846	0.2927	0.1529	0.057*
C2	0.75124 (18)	0.7738 (5)	0.1809 (2)	0.0370 (6)
H2A	0.7053	0.6884	0.1127	0.055*
H2B	0.7923	0.8614	0.1441	0.055*
H2C	0.7194	0.8822	0.222	0.055*
C3	0.89848 (18)	0.7245 (5)	0.4417 (2)	0.0403 (7)
H3A	0.863	0.8458	0.4686	0.06*
H3B	0.9492	0.7967	0.4177	0.06*
H3C	0.9241	0.6152	0.5126	0.06*
C4	0.73868 (16)	0.3931 (4)	0.3582 (2)	0.0290 (6)
C5	0.68058 (15)	0.2953 (4)	0.3936 (2)	0.0269 (5)
C6	0.61124 (15)	0.1820 (4)	0.4346 (2)	0.0259 (5)
C7	0.57692 (14)	0.2577 (4)	0.5332 (2)	0.0235 (5)
H7	0.5956	0.394	0.584	0.028*
C8	0.50819 (15)	0.0909 (4)	0.5434 (2)	0.0250 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0330 (4)	0.0353 (4)	0.0331 (4)	−0.0076 (3)	0.0165 (3)	−0.0039 (3)
Si1	0.0244 (4)	0.0256 (4)	0.0260 (4)	−0.0033 (3)	0.0113 (3)	0.0012 (3)
C1	0.0400 (15)	0.0373 (15)	0.0427 (15)	0.0019 (12)	0.0226 (13)	0.0000 (12)
C2	0.0428 (15)	0.0325 (14)	0.0362 (14)	0.0019 (12)	0.0132 (12)	0.0056 (12)
C3	0.0372 (15)	0.0473 (17)	0.0367 (14)	−0.0116 (13)	0.0119 (12)	−0.0053 (13)
C4	0.0293 (13)	0.0317 (14)	0.0273 (12)	−0.0017 (11)	0.0105 (10)	0.0005 (10)
C5	0.0255 (12)	0.0291 (13)	0.0262 (12)	−0.0006 (11)	0.0083 (10)	0.0012 (10)
C6	0.0215 (12)	0.0268 (13)	0.0277 (12)	−0.0033 (10)	0.0055 (10)	0.0041 (10)
C7	0.0188 (11)	0.0307 (13)	0.0218 (11)	−0.0074 (10)	0.0076 (9)	0.0041 (10)
C8	0.0230 (12)	0.0271 (12)	0.0244 (11)	−0.0010 (10)	0.0069 (10)	0.0014 (9)

Geometric parameters (Å, º)

S1—C8^i	1.718 (2)	C8—S1^i	1.718 (2)
S1—C6	1.742 (2)	C1—H1A	0.98
Si1—C4	1.840 (2)	C1—H1B	0.98
Si1—C2	1.853 (3)	C1—H1C	0.98
Si1—C1	1.858 (3)	C2—H2A	0.98
Si1—C3	1.863 (3)	C2—H2B	0.98
C4—C5	1.207 (3)	C2—H2C	0.98
C5—C6	1.424 (3)	C3—H3A	0.98
C6—C7	1.409 (3)	C3—H3B	0.98
C7—C8	1.444 (3)	C3—H3C	0.98
C8—C8^i	1.381 (4)	C7—H7	0.95
C8^i—S1—C6	90.76 (11)	Si1—C1—H1C	109.47
C4—Si1—C2	107.07 (11)	H1A—C1—H1B	109.51

C4—Si1—C1	108.86 (12)	H1A—C1—H1C	109.49
C2—Si1—C1	111.67 (12)	H1B—C1—H1C	109.46
C4—Si1—C3	107.67 (11)	Si1—C2—H2A	109.43
C2—Si1—C3	110.11 (13)	Si1—C2—H2B	109.49
C1—Si1—C3	111.28 (13)	Si1—C2—H2C	109.50
C5—C4—Si1	175.1 (2)	H2A—C2—H2B	109.42
C4—C5—C6	179.3 (3)	H2A—C2—H2C	109.49
C7—C6—C5	126.2 (2)	H2B—C2—H2C	109.49
C7—C6—S1	114.33 (16)	Si1—C3—H3A	109.46
C5—C6—S1	119.50 (17)	Si1—C3—H3B	109.48
C6—C7—C8	107.8 (2)	Si1—C3—H3C	109.47
C8^i—C8—C7	115.1 (2)	H3A—C3—H3B	109.47
C8^i—C8—S1^i	112.0 (2)	H3A—C3—H3C	109.44
C7—C8—S1^i	132.87 (18)	H3B—C3—H3C	109.51
Si1—C1—H1A	109.44	C6—C7—H7	126.19
Si1—C1—H1B	109.46	C8—C7—H7	126.05

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.