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Crystal structure of 1,3,5-tris(thien-2-yl)benzene, $C_{18}H_{12}S_3$

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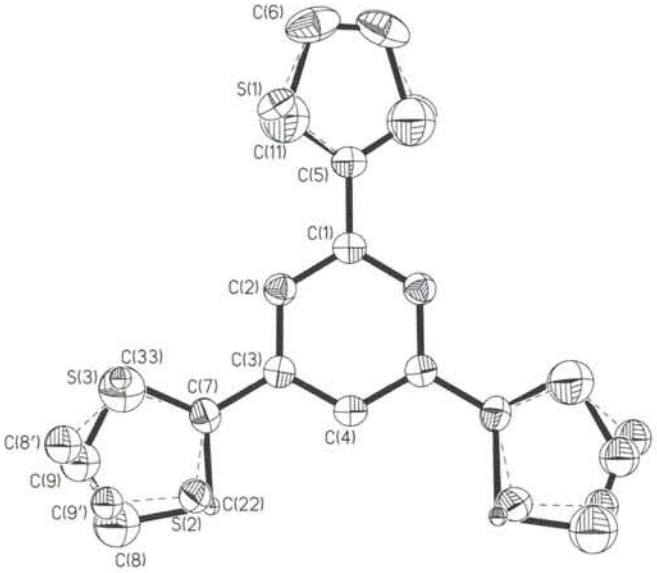

Abstract

$C_{18}H_{12}S_3$, orthorhombic, *Pbcn* (No. 60), $a = 16.052(2)$ Å, $b = 11.523(1)$ Å, $c = 8.236(1)$ Å, $V = 1523.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.076$, $wR_{ref}(F^2) = 0.250$, $T = 296$ K.

Source of material

The title compound was synthesized by modification of cross-coupling reaction of tributyl(2-thienyl)stannane and 1,3,5-tribromobenzene [1]. The starting tributyl(2-thienyl)-stannane was prepared as previously described in the literature [2]. To a solution of tributyl(2-thienyl)stannane (5.00 g, 13.4 mmol) in 20 mL of anhydrous toluene were added 1,3,5-tribromobenzene (1.4 g, 4.45 mmol) and LiCl (2.80 g, 65.6 mmol) The reaction mixture was stirred at room temperature under N_2 inert atmosphere for 10 min. To a solution of reaction mixture was added $PdCl_2(PPh_3)_2$ (0.23 g, 0.33 mmol) and the mixture was refluxed for 24 h. The solvent was evaporated under vacuum and then the solid residue was chromatographed on silicagel column eluting hexanes/CH_2Cl_2 (4:1) mixture. The collected eluent was removed under vacuum to give white product (0.75 g, 2.31 mmol, 52 % yield) of 1,3,5-tris(thieny-2-yl)benzene (**I**). Single crystals of **I** suitable for X-ray diffraction studies were grown from ethanol solution by slow cooling to 253 K for 4 days.

Experimental details

The S(2) and S(3) thienyl rings were refined with idealized geometries. The bonds were constrained as follows. Bond S(2)—C(7) was calculated as 0.6 × 1.714 Å + 0.4 × 1.370 Å = 1.576 Å, taking into account the disorder ratio. The S(3)—C(7) bond was estimated to be 0.4 × 1.714 Å + 0.6 × 1.370 Å = 1.508 Å by the same method. Other S—C distances were constrained to 1.714 Å and the C(α)—C(β) bond distances to 1.370 Å and the C(β)—C(β) bond distances to 1.424 Å. H atoms of the thienyl-rings were not localized.

Discussion

The thienyl rings in the title compound are not co-planar with the plane of the phenyl ring. The torsion angles S(1)–C(5)–C(1)–C(2) and S(2)–C(7)–C(3)–C(2) were found to be 21.4(2)° and –23.1(6)°, respectively. However the thienyl rings are nearly planar with an average standard deviation from planarity of the ring atoms of 0.02 Å. The molecule occupies a crystallographic two-fold axis passing through atoms C(1), C(4), C(5), and the middle of the bond C(6)–C(6a). Thus, only one half of the molecule is symmetry independent. As a result, a disorder of the S(1) thienyl ring over two positions in a 50:50 ratio is introduced. The positions of atoms S(1) and S(1a) are occupied by sulfur atoms 50% of the time and 50% of the time they are occupies by carbons. Consequently, the observed S(1)—C(5) distance (1.608(7) Å) is the average between a single S—C bond (1.714 Å) and a C=C double bond (1.370 Å). Additionally, there is positional disorder in the orientation of the S(2) thienyl moiety. It is disordered in a 60:40 ratio over two positions. The position of atom S(2) is occupied by a sulfur atom 60% of the time, and the positions of atoms C(8), C(9), and C(33) are occupied by carbon atoms 60% of the time as well. The positions of atoms C(8′), C(9′) and C(22) are occupied by carbon atoms 40% of the time while the position of atom S(3) is occupied 40% of the time by a sulfur atom.

Table 1. Data collection and handling.

Crystal:	colorless rhombus, size 0.27 × 0.39 × 0.42 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.74 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ and ω scans
$2\theta_{max}$:	51.34°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1442, 1442
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 831
$N(param)_{refined}$:	109
Programs:	SADABS [3], SHELXTL [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
C(11)	8*d*	0.50	0.566(2)	–0.100(2)	0.221(4)	0.14(1)
C(22)	8*d*	0.40	0.6044(9)	0.486(1)	0.018(2)	0.014(3)
C(33)	8*d*	0.60	0.7158(5)	0.2852(8)	0.037(1)	0.025(2)
H(2)	8*d*		0.6028	0.1173	0.112	0.062
H(4)	4*c*		1/2	0.4176	1/4	0.061
C(8)	8*d*	0.40	0.6960(7)	0.507(2)	–0.069(3)	0.112(9)
C(9)	8*d*	0.40	0.742(1)	0.407(1)	–0.055(2)	0.075(5)
C(8′)	8*d*	0.60	0.7587(5)	0.3808(7)	–0.062(1)	0.076(4)
C(9′)	8*d*	0.60	0.7065(3)	0.4748(8)	–0.072(1)	0.057(3)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8*d*	0.50	0.5795(3)	–0.1118(4)	0.2139(6)	0.062(2)	0.049(2)	0.071(2)	0.016(1)	0.000(2)	–0.005(1)
S(2)	8*d*	0.60	0.6207(2)	0.4691(3)	0.0056(5)	0.057(2)	0.058(2)	0.084(2)	0.004(1)	0.009(2)	0.007(2)
S(3)	8*d*	0.40	0.7123(4)	0.2978(6)	0.029(1)	0.105(5)	0.115(6)	0.153(7)	–0.001(3)	0.012(4)	0.007(3)
C(1)	4*c*		1/2	0.0953(5)	1/4	0.050(4)	0.053(4)	0.047(4)	0	–0.007(3)	0
C(2)	8*d*		0.5616(3)	0.1576(4)	0.1681(5)	0.054(3)	0.052(3)	0.050(3)	0.001(2)	0.000(2)	–0.004(2)
C(3)	8*d*		0.5631(3)	0.2784(4)	0.1681(5)	0.049(3)	0.051(3)	0.046(2)	0.001(2)	–0.004(2)	0.001(2)
C(4)	4*c*		1/2	0.3369(5)	1/4	0.054(4)	0.049(4)	0.051(4)	0	–0.007(3)	0
C(5)	4*c*		1/2	–0.0310(5)	1/4	0.062(5)	0.047(4)	0.052(4)	0	–0.004(3)	0
C(6)	8*d*		0.5386(4)	–0.2323(5)	0.2309(8)	0.161(8)	0.065(3)	0.064(4)	0.031(3)	–0.024(5)	–0.007(3)
C(7)	8*d*		0.6279(3)	0.3428(3)	0.0790(5)	0.050(3)	0.064(3)	0.054(3)	–0.006(2)	0.002(2)	–0.003(2)

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