

Muhammad S. Khan,^a Birte Ahrens,^b Mary F. Mahon,^b Louise Male^{b*} and Paul R. Raithby^b^aDepartment of Chemistry, College of Science, Sultan Qaboos University, PO Box 36, Al Khod 123, Sultanate of Oman, and ^bDepartment of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, England

Correspondence e-mail: chplm@bath.ac.uk

Key indicators

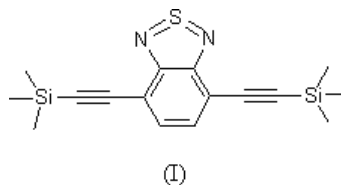
Single-crystal X-ray study
 $T = 170\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
Disorder in main residue
 R factor = 0.045
 wR factor = 0.116
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

4,7-Bis(trimethylsilylethynyl)-2,1,3-benzothiadiazole

The title compound, $\text{C}_{16}\text{H}_{20}\text{N}_2\text{SSi}_2$ is a rigid-rod protected dialkyne. It is used as a model species for platinum-containing compounds of which it is a precursor. Such compounds are of interest due to the extended π -conjugation exhibited through the heteroaromatic linker unit in the backbone. The molecule is pseudo-linear, with a planar central benzothiadiazole group.

Comment

In this paper, we report the structural characterization of the title compound, (I), which is a TMS-protected rigid-rod dialkyne and a precursor of the platinum(II) di-yne species *trans*- $[(\text{Et}_3\text{P})_2(\text{Ph})\text{Pt}-\text{C}\equiv\text{C}-R-\text{C}\equiv\text{C}-\text{Pt}(\text{Ph})(\text{Et}_3\text{P})_2]$ ($R = 2,1,3$ -benzothiadiazole-4,7-diyl; Kahn *et al.*, 2002). This type of platinum-containing species forms the building block for a rigid-rod organometallic polymer of general formula *trans*- $[(\text{Et}_2)\text{Pt}-\text{C}\equiv\text{C}-R-\text{C}\equiv\text{C}-]_{\infty}$ ($R =$ aromatic or heteroaromatic linker unit). Such poly-yne are of interest due to the extended π -conjugation exhibited along the backbone and the resulting optical emission properties (Wittmann *et al.*, 1994; Beljonne *et al.*, 1996; Younus *et al.*, 1998; Chawdhury *et al.*, 1998, 1999; Wilson *et al.*, 2000, 2001, 2002). The various precursors to these species are studied as models of the molecular and electronic properties and structure–property relationships in the polymers.



The central benzothiadiazole ring system of the molecule is planar and the backbone is pseudo-linear. It is assumed that close intermolecular interactions in the structure are prevented by the bulk of the trimethylsilyl groups. The molecules stack along the b axis, with a distance of 5.7385 (6) Å between adjacent moieties.

Experimental

4,7-Bis(trimethylsilylethynyl)-2,1,3-benzothiadiazole was synthesized by the following procedure. Catalytic amounts of CuI (10 mg, 0.05 mmol), Pd(OAc)₂ (10 mg, 0.04 mmol) and PPh₃ (30 mg, 0.11 mmol) were added to a solution of 4,7-dibromo-2,1,3-benzothiadiazole (1.52 g, 5.17 mmol) in NH⁺Pr₂/THF (50 ml, 1:4 v/v) under nitrogen. The solution was stirred for 30 min at room temperature and then trimethylsilylethyne (1.27 g, 12.93 mmol) was added at room temperature to the vigorously stirred solution; during the addition, a white precipitate formed. The reaction mixture was stirred at reflux for 2 h and the completion of the reaction was determined by silica

Received 24 September 2002

Accepted 1 October 2002

Online 5 October 2002

thin-layer chromatography and IR spectroscopy. After cooling to room temperature, the mixture was filtered to eliminate the ammonium salt and the solvent mixture was removed under vacuum. The residue was then purified by silica-column chromatography, eluting with hexane/CH₂Cl₂ (1:2 v/v), to yield a light-yellow solid, *i.e.* the target compound, in 78% yield (1.32 g).

Crystal data

C₁₆H₂₀N₂SSi₂
M_r = 328.58
 Monoclinic, *P*2₁/*n*
a = 17.623 (3) Å
b = 5.7385 (6) Å
c = 20.089 (4) Å
 β = 112.061 (2)°
V = 1882.9 (5) Å³
Z = 4

D_x = 1.159 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 9092 reflections
 θ = 2.9–25.0°
 μ = 0.30 mm⁻¹
T = 170 (2) K
 Plate, pale yellow
 0.23 × 0.18 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 5933 measured reflections
 3293 independent reflections
 2565 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.026
 θ_{\max} = 25.1°
h = -20 → 20
k = -5 → 6
l = -23 → 22

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.045
wR (*F*²) = 0.116
S = 1.03
 3293 reflections
 243 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.8463P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1–N2	1.6141 (19)	C5'–C6	1.42 (3)
S1–N1	1.6169 (19)	C6–C7	1.369 (3)
N1–C11	1.348 (3)	C6–C11	1.428 (3)
N2–C10	1.344 (3)	C7–C8	1.413 (3)
Si2–C13	1.842 (2)	C8–C9	1.371 (3)
Si1–C4	1.832 (10)	C9–C10	1.428 (3)
C4–C5	1.219 (19)	C9–C12	1.440 (3)
C5–C6	1.460 (18)	C10–C11	1.432 (3)
Si1'–C4'	1.855 (14)	C12–C13	1.203 (3)
C4'–C5'	1.17 (3)		
N2–S1–N1	101.28 (9)	C4'–C5'–C6	172.8 (16)
C5–C4–Si1	178.0 (7)	C13–C12–C9	175.4 (3)
C4–C5–C6	176.7 (9)	C12–C13–Si2	175.4 (2)
C5'–C4'–Si1'	169.4 (12)		
N2–S1–N1–C11	0.35 (16)	C8–C9–C10–N2	-177.7 (2)
N1–S1–N2–C10	-0.16 (16)	C7–C6–C11–N1	177.6 (2)
C6–C7–C8–C9	0.7 (5)		

Aromatic and methyl H atoms were constrained as riding atoms fixed to their parent atoms at distances of 0.95 and 0.98 Å, respectively. The isotropic displacement parameters were fixed to 1.2*U*_{eq} of that of the parent atom for aromatic and 1.5*U*_{eq} for methyl H atoms. Atoms C1–C5 and Si1 are disordered over two sites with occupancies of 60% and 40%, respectively.

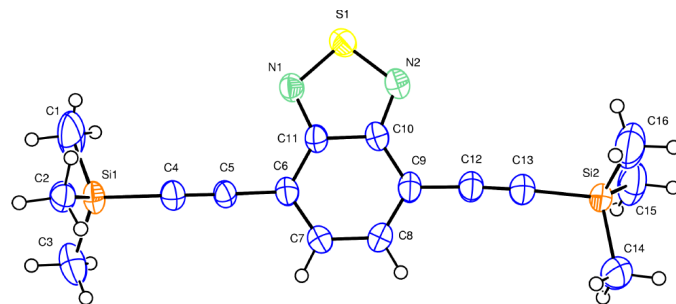


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms C1–C5 and Si1 are disordered over two sites, with only one orientation of this group being shown for clarity.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank the Cambridge Crystallographic Data Centre for funding.

References

- Beljonne, D., Wittmann, H. F., Köhler, A., Graham, S., Younus, M., Lewis, J., Raithby, P. R., Kahn, M. S., Friend, R. H. & Bredas, J. L. (1996). *J. Chem. Phys.* **105**, 3868–3877.
- Chawdhury, N., Köhler, A., Friend, R. H., Younus, M., Long, N. J., Raithby, P. R. & Lewis, J. (1998). *Macromolecules*, **31**, 722–727.
- Chawdhury, N., Köhler, A., Friend, R. H., Wong, W.-Y., Younus, M., Raithby, P. R., Lewis, J., Corcoran, T. C., Al-Mandhary, M. R. A. & Kahn, M. S. (1999). *J. Chem. Phys.* **110**, 4963–4970.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Kahn, M. S., Al-Suti, M. K., Al-Mandhary, M. R. A., Ahrens, B., Bjernemose, J. K., Mahon, M. F., Male, L., Raithby, P. R., Friend, R. H., Köhler, A. & Wilson, J. S. (2002). Unpublished results.
- Nonius (1997). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Wilson, J. S., Köhler, A., Friend, R. H., Al-Suti, M. K., Al-Mandhary, M. R. A., Kahn, M. S. & Raithby, P. R. (2000). *J. Chem. Phys.* **113**, 7627–7634.
- Wilson, J. S., Chawdhury, N., Köhler, A., Friend, R. H., Al-Mandhary, M. R. A., Kahn, M. S., Younus, M. & Raithby, P. R. (2001). *J. Am. Chem. Soc.* **123**, 9412–9417.
- Wilson, J. S., Dhoot, A. S., Seeley, A. J. A. B., Kahn, M. S., Köhler, A. & Friend, R. H. (2002). *Nature (London)*, **413**, 828–831.
- Wittmann, H. F., Friend, R. H., Kahn, M. S. & Lewis, J. (1994). *J. Chem. Phys.* **101**, 2693–2698.
- Younus, M., Köhler, A., Cron, S., Chawdhury, N., Al-Mandhary, M. R. A., Kahn, M. S., Lewis, J., Long, N. J., Friend, R. H. & Raithby, P. R. (1998). *Angew. Chem. Int. Ed.* **37**, 3036–3039.