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(*R*)-2,2′-Bis{[5-(2-phenylethynyl)thienyl]-ethynyl}-1,1′-binaphthyl

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean *σ*(C–C) = 0.002 Å
R factor = 0.030
wR factor = 0.094
Data-to-parameter ratio = 8.7

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

The crystal structure of the title compound, $C_{48}H_{26}S_2$, has been determined in the monoclinic space group *C*2 at 123 K. The compound possesses C_2 symmetry, the crystallographic twofold axis passing through the mid-point of the bond connecting the two naphthyl moieties. The dihedral angle between the two naphthyl groups is 69.3 (3)°, the dihedral angle between the phenyl and thienylene groups is 83.2 (3)°, and the dihedral angle between the thienylene and naphthyl groups is 8.7 (3)°.

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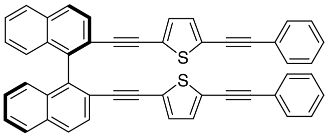
Comment

Phenylene–ethynylenes have received great attention as organic photoluminescent (Kokil *et al.*, 2002) and electroluminescent compounds (Kraft *et al.*, 1998) and a number of phenylene–ethynylenes have been prepared (Bunz, 2001). We have been intrigued by such features of phenylene–ethynylenes, and we have successfully prepared acetylenes bearing various substituents (Orita *et al.*, 1999), a highly strained acetylenic cyclophane (Orita, Hasegawa, Nakano & Otera, 2002) and optically active acetylenic cyclophanes (Orita, Hasegawa, An *et al.*, 2002). Furthermore, it is recognized that thiophene derivatives serve as conducting organic materials and various types of oligo- and polythiophenes have been reported (Miller & Mann, 1996). We have prepared an optically active phenylene–ethynylene-bearing thiophenylene, *viz.* (I), in expectation of a new function of phenylene–ethynylene derivatives as a new category of photo- and electroluminescent compounds. We describe here the structural features of (I) in the solid state.



(I)

(*R*)-1,1′-Binaphthyl was employed as a chiral center and, in the crystal structure, the dihedral angle between the two naphthyl groups is 69.3 (3)°. The title compound shows C_2 symmetry, the crystallographic twofold axis passing through the mid-point of the C1—C1′ bond (Fig. 1). The two arylene–ethynylenes are oriented in opposite directions, showing no intramolecular interaction with each other. Although both types of acetylenes are conjugated to arenes, the bond lengths C17—C18 and C11—C12, 1.201 (2) and 1.2018 (17) Å, respectively, are in good agreement with values observed in cyclic acetylenes which we have prepared earlier (Orita, Jiang *et al.*, 2002). The dihedral angles between phenyl and thienylene and between thienylene and naphthylene are

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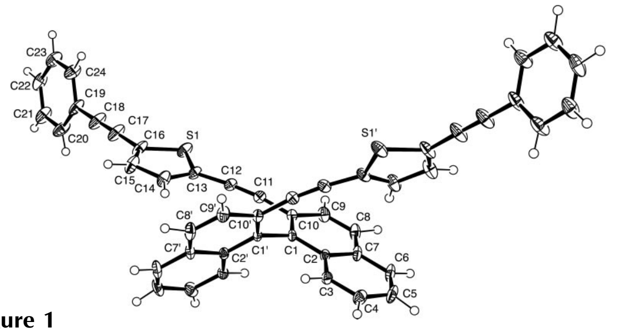

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

83.2 (3) and 8.7 (3)°, respectively, showing that the three aromatic ring systems are not completely conjugated.

Experimental

A mixture of Pd(PPh$_3$)$_4$ (91.3 mg, 0.079 mmol), CuI (15.0 mg, 0.079 mmol), 2-bromo-5-(phenylethylyne)thiophene (500 mg, 1.90 mmol), (*R*)-2,2′-ethynyl-1,1′-binaphthyl (240 mg, 0.791 mmol) and ^{i}Pr$_2$NH (3 ml) in toluene (20 ml) was heated under an argon atmosphere at 318 K for 15 h. After the usual work-up with NH$_4$Cl/CHCl$_3$, the organic layer was dried over MgSO$_4$, and the solvents were removed under reduced pressure. The resulting residue was purified by chromatography on silica gel (hexane—CH$_2$Cl$_2$ 4:1, R_F = 0.23) to give 429.3 mg of the title compound, (I), as a yellow solid (81% yield); ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.51 (*d, J* = 3.8 Hz, 2H), 6.94 (*d, J* = 3.8 Hz, 2H), 7.40–7.30 (*m*, 10H), 7.48–7.46 (*m*, 4H), 7.54–7.51 (*m*, 2H), 7.76 (*d, J* = 8.2 Hz, 2H), 7.99 (*dd, J* = 8.2, *J* = 6.7 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 82.4, 86.4, 93.9, 94.2, 121.1, 122. 6, 124.4, 124.5, 126.5, 126.8, 127.0, 127.6, 128.1, 128.2, 128.3, 128.6, 131.4, 131.5, 131.6, 132.5, 133.1, 140.0; elemental analysis calculated (%) for $C_{48}H_{26}S_2$: C 86.45, H 3.93, found: C 86.29 H 3.66.

Crystal data

$C_{48}H_{26}S_2$
$M_r = 666.85$
Monoclinic, *C*2
$a = 12.2484$ (1) Å
$b = 12.6553$ (1) Å
$c = 11.5031$ (9) Å
$\beta = 102.407$ (5)°
$V = 1741.4$ (1) Å^3
$Z = 2$

$D_x = 1.272$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 3933 reflections
$\theta = 2.3$–25.0°
$\mu = 0.19$ mm^{-1}
$T = 123.1$ K
Cube, yellow
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku RAXIS-IV diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.963$, $T_{\max} = 1.000$
6879 measured reflections
3505 independent reflections
3501 reflections with $F^2 > 2\sigma(F^2)$

$R_{\rm int} = 0.022$
$\theta_{\max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -16 \rightarrow 15$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 20 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.094$
$S = 1.18$
2081 reflections
240 parameters
All H-atom parameters refined

$w = 1/[0.0016F_o^2 + \sigma^2(F_o) + 0.5]/(4F_o^2)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}
Absolute structure: Flack (1983), 1592 Friedel pairs
Flack parameter = 0.07 (4)

Table 1
Selected geometric parameters (Å, °).

S1—C13	1.7274 (12)	C14—C15	1.4206 (18)
S1—C16	1.7282 (13)	C15—C16	1.377 (2)
C10—C11	1.4302 (17)	C16—C17	1.4252 (17)
C11—C12	1.2018 (17)	C17—C18	1.201 (2)
C12—C13	1.4220 (16)	C18—C19	1.4314 (18)
C13—C14	1.3768 (18)		
S1—C13—C12	121.95 (9)	C13—C14—C15	113.15 (12)
S1—C13—C14	111.21 (9)	C14—C15—C16	112.13 (12)
C13—S1—C16	91.76 (6)	C15—C16—C17	128.99 (13)
S1—C16—C17	119.22 (11)	C16—C17—C18	177.12 (13)
S1—C16—C15	111.74 (9)	C17—C18—C19	177.94 (17)
C9—C10—C11	120.24 (11)	C18—C19—C20	119.91 (14)
C10—C11—C12	172.28 (13)	C18—C19—C24	120.79 (13)
C11—C12—C13	173.98 (13)	C1—C10—C9	120.3 (1)
C12—C13—C14	126.82 (11)	C1—C10—C11	119.4 (1)
C16—S1—C13—C12	178.1 (1)	C17—C16—C15—C14	177.5 (2)
C16—S1—C13—C14	−0.2 (1)	C2—C1—C10—C11	178.6 (1)
C13—S1—C16—C17	−177.6 (1)	C8—C9—C10—C11	−179.8 (1)
C13—S1—C16—C15	0.1 (1)	C8—C9—C10—C1	−1.3 (2)
S1—C13—C14—C15	0.3 (1)	C18—C19—C20—C21	177.2 (1)
C12—C13—C14—C15	−177.9 (1)	C16—C15—C14—C13	−0.3 (2)
S1—C16—C15—C14	0.1 (1)		

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Rigaku, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); 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: *CrystalStructure* (Molecular Structure Corporation and Rigaku, 2001).

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