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3′-(Methylsulfanyl)biphenyl-4-carbonitrile

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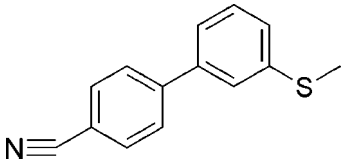
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.097; data-to-parameter ratio = 18.3.

In the title compound, $C_{14}H_{11}NS$, the two benzene rings make a dihedral angle of 22.0 (2)°. The cyano group and the S atom are coplanar with their corresponding benzene rings.

Related literature

For related literature, see: Gans *et al.* (1990); Khanna *et al.* (2000); Robbins *et al.* (2003).



Experimental

Crystal data

$C_{14}H_{11}NS$
M_r = 225.30
Orthorhombic, $P2_12_12_1$
a = 7.2200 (14) Å
b = 11.961 (2) Å
c = 12.936 (3) Å
V = 1117.2 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 113 (2) K
0.14 × 0.12 × 0.08 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.965, T_{max} = 0.980
14124 measured reflections
2670 independent reflections
2539 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.097
S = 1.09
2670 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983), with 1118 Friedel Pairs
Flack parameter: 0.04 (10)

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalStructure* (Rigaku/MSC, 2004); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2450).

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supplementary materials

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Comment

Aryl compounds with a methylthio group are of interest as pesticide and synthetic intermediates used in the preparation of many pharmaceuticals (Robbins, *et al.*, 2003). The methylthio group can be easily oxidized to form sulfinyl or sulfonyl groups, which are useful groups in pharmaceuticals (Gans, *et al.*, 1990; Khanna, *et al.*, 2000). Here, we report the synthesis and crystal structure of the title compound, (I).

The title compound of (I), contains two benzene rings and they make a dihedral angle of 22.0 (2)°. the torsion angles of C1—S1—C2—C3 and C1—S1—C2—C7 are 5.6 (2) and 174.60 (15)°, respectively, indicating that S atom don't significantly deviate from the benzene ring plane (C2—C7). The *p*-π conjugation of S atom with the benzene ring affect the bond distance S1—C2 [1.767 (2) Å] which is shorter than S1—C1 [1.7991 (19) Å].

Experimental

A mixture of 3-methylthiophenylboronic acid (1.327 mmol), 4-bromobenzonitrile (0.8845 mmol), K_2CO_3 (2.657 mmol) and POPd (0.00177 mmol, 0.2 mol %) was stirred and refluxed in 2 ml of dioxane for 3 h. The reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with EtOAc. The combined organic layers were washed with brine and dried over $MgSO_4$, and the solvents were removed under vacuum. The residue was purified by chromatography on silica gel eluting with hexane/EtOAc (60:1 *v*/*v*) to give the target product as white acicular crystal in 99.7% yield (m.p.337 K). Spectroscopic analysis: IR (KBr): 2230 cm^{-1}. ^1H NMR (500 MHz, Chloroform-d1, TMS): δ 2.54 (s, 3H), 7.31 (d, 1H, J= 7.8 Hz), 7.34 (d, 1H, J= 7.8 Hz), 7.39–7.42 (t, 1H, J= 7.8 Hz), 7.45 (s, 1H), 7.67 (d, 2H, J= 8.4 Hz), 7.73 (d, 2H, J= 8.3 Hz). ^{13}C NMR (125 MHz, TMS): δ 15.8, 124., 125.4, 126.7, 127.9, 129.6, 139.5, 139.9, 147.2, 147.3; HRMS (EI): M^+, found 225.0616. $C_{14}H_{11}NS$ requires 225.0612. Crystals of (I) suitable for single-crystal X-ray analysis were grown by slow evaporation of a solution in chloroform-ethanol (1:1 *v*/*v*).

Refinement

All H atoms were positioned geometrically and refined using a riding on their parent atoms, with C—H = 0.95–0.98Å and $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$.

Figures

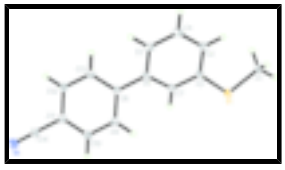

Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level.

3'-(Methylsulfanyl)biphenyl-4-carbonitrile

Crystal data

$C_{14}H_{11}NS$	$D_x = 1.340$ Mg m^{-3}
$M_r = 225.30$	Melting point: 337 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 3597 reflections
$a = 7.2200$ (14) Å	$\theta = 2.3$–27.8º
$b = 11.961$ (2) Å	$\mu = 0.26$ mm^{-1}
$c = 12.936$ (3) Å	$T = 113$ (2) K
$V = 1117.2$ (4) Å^3	Prism, colourless
$Z = 4$	0.14 × 0.12 × 0.08 mm
$F_{000} = 472$	

Data collection

Rigaku Saturn diffractometer	2670 independent reflections
Radiation source: rotating anode	2539 reflections with $I > 2\sigma(I)$
Monochromator: confocal	$R_{int} = 0.046$
$T = 113$(2) K	$\theta_{max} = 27.9$º
ω and φ scans	$\theta_{min} = 2.3$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.965$, $T_{max} = 0.980$	$k = -15 \rightarrow 15$
14124 measured reflections	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.3196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
2670 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
146 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1118 Friedel Pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.04 (10)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.24370 (8)	0.21096 (4)	0.38537 (4)	0.02390 (14)
C6	0.1139 (2)	0.30649 (16)	0.09659 (14)	0.0174 (4)
C2	0.1735 (3)	0.29709 (17)	0.28158 (15)	0.0190 (4)
N1	0.1321 (3)	0.04988 (16)	−0.37872 (15)	0.0304 (4)
C13	0.1450 (3)	0.31419 (16)	−0.09653 (15)	0.0209 (4)
H13	0.1649	0.3925	−0.0914	0.025*
C11	0.1171 (3)	0.14894 (18)	−0.20058 (15)	0.0203 (4)
C8	0.1125 (3)	0.25204 (17)	−0.00672 (16)	0.0179 (4)
C12	0.1485 (3)	0.26366 (17)	−0.19279 (16)	0.0218 (4)
H12	0.1721	0.3068	−0.2530	0.026*
C5	0.0609 (3)	0.41861 (16)	0.10827 (16)	0.0211 (4)
H5	0.0211	0.4604	0.0499	0.025*
C9	0.0812 (3)	0.13761 (17)	−0.01641 (16)	0.0199 (4)
H9	0.0587	0.0942	0.0438	0.024*
C1	0.2520 (4)	0.30445 (16)	0.49421 (15)	0.0274 (4)
H1A	0.3363	0.3665	0.4789	0.041*
H1B	0.2966	0.2639	0.5552	0.041*
H1C	0.1277	0.3338	0.5079	0.041*
C4	0.0664 (3)	0.46838 (17)	0.20489 (16)	0.0243 (5)
H4	0.0320	0.5447	0.2119	0.029*
C7	0.1708 (3)	0.24753 (16)	0.18386 (15)	0.0184 (4)
H7	0.2086	0.1719	0.1767	0.022*
C14	0.1240 (3)	0.09457 (18)	−0.30001 (16)	0.0231 (4)
C10	0.0824 (3)	0.08612 (16)	−0.11220 (16)	0.0219 (4)
H10	0.0595	0.0081	−0.1176	0.026*
C3	0.1214 (3)	0.40857 (17)	0.29177 (16)	0.0219 (4)
H3	0.1234	0.4436	0.3577	0.026*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0307 (3)	0.0233 (2)	0.0177 (2)	0.0006 (2)	−0.0026 (2)	−0.00141 (19)

C6	0.0115 (9)	0.0194 (9)	0.0211 (10)	−0.0031 (7)	0.0002 (7)	−0.0002 (8)
C2	0.0162 (9)	0.0209 (9)	0.0199 (9)	−0.0020 (8)	0.0001 (7)	−0.0022 (8)
N1	0.0353 (11)	0.0311 (10)	0.0248 (10)	0.0022 (8)	−0.0014 (9)	−0.0029 (8)
C13	0.0210 (10)	0.0188 (10)	0.0230 (11)	−0.0006 (8)	−0.0012 (8)	−0.0001 (8)
C11	0.0157 (10)	0.0247 (10)	0.0203 (10)	0.0027 (8)	−0.0020 (8)	−0.0014 (8)
C8	0.0145 (9)	0.0210 (9)	0.0181 (10)	0.0003 (7)	−0.0015 (8)	−0.0010 (8)
C12	0.0205 (11)	0.0238 (10)	0.0210 (10)	0.0004 (8)	−0.0017 (8)	0.0032 (8)
C5	0.0192 (10)	0.0195 (9)	0.0247 (10)	0.0005 (8)	0.0001 (9)	0.0012 (9)
C9	0.0196 (10)	0.0203 (10)	0.0199 (10)	0.0005 (8)	0.0002 (8)	0.0014 (8)
C1	0.0327 (11)	0.0308 (11)	0.0186 (9)	−0.0034 (11)	0.0009 (10)	−0.0038 (8)
C4	0.0222 (11)	0.0191 (10)	0.0315 (12)	0.0024 (9)	−0.0004 (9)	−0.0038 (9)
C7	0.0146 (9)	0.0208 (9)	0.0198 (10)	−0.0017 (8)	0.0016 (7)	−0.0012 (8)
C14	0.0205 (10)	0.0247 (10)	0.0241 (11)	0.0032 (8)	−0.0030 (8)	0.0009 (9)
C10	0.0231 (10)	0.0182 (9)	0.0243 (10)	0.0019 (8)	−0.0005 (9)	−0.0019 (9)
C3	0.0211 (10)	0.0224 (10)	0.0221 (10)	0.0020 (8)	0.0011 (8)	−0.0055 (8)

Geometric parameters (Å, °)

S1—C2	1.767 (2)	C8—C9	1.393 (3)
S1—C1	1.7991 (19)	C12—H12	0.9500
C6—C7	1.393 (3)	C5—C4	1.385 (3)
C6—C5	1.403 (3)	C5—H5	0.9500
C6—C8	1.487 (3)	C9—C10	1.384 (3)
C2—C3	1.392 (3)	C9—H9	0.9500
C2—C7	1.396 (3)	C1—H1A	0.9800
N1—C14	1.151 (3)	C1—H1B	0.9800
C13—C12	1.384 (3)	C1—H1C	0.9800
C13—C8	1.399 (3)	C4—C3	1.390 (3)
C13—H13	0.9500	C4—H4	0.9500
C11—C10	1.391 (3)	C7—H7	0.9500
C11—C12	1.394 (3)	C10—H10	0.9500
C11—C14	1.442 (3)	C3—H3	0.9500
C2—S1—C1	104.00 (10)	C10—C9—C8	121.13 (19)
C7—C6—C5	118.50 (18)	C10—C9—H9	119.4
C7—C6—C8	120.58 (17)	C8—C9—H9	119.4
C5—C6—C8	120.91 (18)	S1—C1—H1A	109.5
C3—C2—C7	119.26 (19)	S1—C1—H1B	109.5
C3—C2—S1	124.36 (15)	H1A—C1—H1B	109.5
C7—C2—S1	116.39 (15)	S1—C1—H1C	109.5
C12—C13—C8	121.20 (18)	H1A—C1—H1C	109.5
C12—C13—H13	119.4	H1B—C1—H1C	109.5
C8—C13—H13	119.4	C5—C4—C3	121.11 (19)
C10—C11—C12	120.09 (19)	C5—C4—H4	119.4
C10—C11—C14	119.72 (19)	C3—C4—H4	119.4
C12—C11—C14	120.18 (19)	C6—C7—C2	121.52 (18)
C9—C8—C13	118.33 (19)	C6—C7—H7	119.2
C9—C8—C6	120.83 (18)	C2—C7—H7	119.2
C13—C8—C6	120.83 (17)	N1—C14—C11	178.7 (2)
C13—C12—C11	119.45 (19)	C9—C10—C11	119.78 (18)

C13—C12—H12	120.3	C9—C10—H10	120.1
C11—C12—H12	120.3	C11—C10—H10	120.1
C4—C5—C6	120.01 (19)	C4—C3—C2	119.58 (19)
C4—C5—H5	120.0	C4—C3—H3	120.2
C6—C5—H5	120.0	C2—C3—H3	120.2
C1—S1—C2—C3	−5.6 (2)	C6—C8—C9—C10	−179.06 (18)
C1—S1—C2—C7	174.60 (15)	C6—C5—C4—C3	−1.0 (3)
C12—C13—C8—C9	−0.8 (3)	C5—C6—C7—C2	0.8 (3)
C12—C13—C8—C6	178.35 (19)	C8—C6—C7—C2	179.90 (17)
C7—C6—C8—C9	30.4 (3)	C3—C2—C7—C6	−1.2 (3)
C5—C6—C8—C9	−150.53 (19)	S1—C2—C7—C6	178.57 (15)
C7—C6—C8—C13	−148.74 (19)	C10—C11—C14—N1	−58 (11)
C5—C6—C8—C13	30.3 (3)	C12—C11—C14—N1	121 (11)
C8—C13—C12—C11	0.7 (3)	C8—C9—C10—C11	0.7 (3)
C10—C11—C12—C13	0.1 (3)	C12—C11—C10—C9	−0.8 (3)
C14—C11—C12—C13	−178.76 (19)	C14—C11—C10—C9	178.1 (2)
C7—C6—C5—C4	0.3 (3)	C5—C4—C3—C2	0.6 (3)
C8—C6—C5—C4	−178.81 (18)	C7—C2—C3—C4	0.5 (3)
C13—C8—C9—C10	0.1 (3)	S1—C2—C3—C4	−179.27 (16)

Fig. 1