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ISSN 2414-3146

3′,4′-Diphenyl-3*H*,4′*H*-spiro[benzo[*b*]thiophene-2,5′-isoxazol]-3-one

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Received 10 July 2018
Accepted 13 July 2018

Edited by J. Simpson, University of Otago, New Zealand

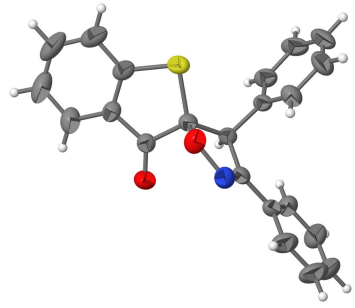
Keywords: crystal structutre; diphenyl; spiro-isoxazolines; isoxazoline; hydrogen bonds; π–π interactions.

CCDC reference: 1855760

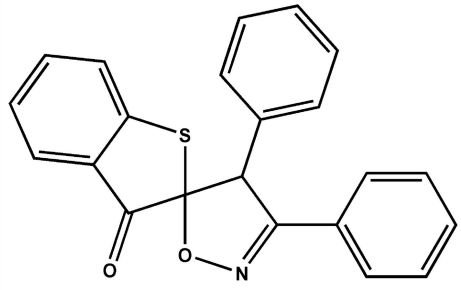
Structural data: full structural data are available from iucrdata.iucr.org

The molecule of the title compound, $C_{22}H_{15}NO_2S$, is built up from a benzothiophene system linked to an isoxazoline ring which is connected to two phenyl rings. The benzothiophene system is essentially planar, while the isoxazoline ring displays an envelope conformation with the spiro C atom as the flap. The mean plane through the isoxazoline ring is slightly inclined to one phenyl ring by 5.74 (13)° and is approximately perpendicular [86.10 (10)°] to the fused ring system and to the other phenyl ring [84.31 (12)°]. In the crystal, molecules are linked together by C—H···O hydrogen bonds and by π–π interactions between the fused ring systems [intercentroid distance = 3.702 (2) Å], forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Molecules containing an isoxazoline framework have been widely used as key building blocks for medicines. Among these compounds, spiroisoxazolines have shown strong bioactivities (Bennani *et al.*, 2007; Al Houari *et al.*, 2008; Hwang *et al.*, 2005). For many years, our laboratory has accumulated much experience in the design and synthesis of heterocyclic systems with isoxazoline and pyrazoline rings through 1,3-dipolar cycloaddition and cyclocondensation reactions (El Yazidi *et al.*, 2003; Bakhouch *et al.*, 2014, 2015, 2017; Mahfoud *et al.*, 2015). In a continuation of our previous work, and in an attempt to evaluate the reactivity of thioaurones with nitrile oxides as a dipole (Boughaleb *et al.*, 2011), we describe herein the reaction of (*Z*)-2-benzylidenbenzo[*b*]thiophen-3(2*H*)-one with benzonitrile oxide in chloroform at low temperature. The title compound was obtained by regiospecific 1,3-dipolar cycloaddition.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C19—H19···O2^{i}	0.93	2.62	3.462 (3)	152
C9—H9···O1^{ii}	0.98	2.66	3.564 (2)	154

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.

The results of the X-ray study were in perfect agreement with IR, ^{1}H NMR and ^{13}C NMR spectroscopic analysis, which confirms the regiospecificity of the reaction.

The isoxazoline ring is linked to two phenyl rings and to a benzothiophene ring system, as shown in Fig. 1. The five-membred ring (N1/O1/C8–C10) adopts an envelope conformation with the spiro C8 atom as the flap. The total puckering amplitude for this ring is $Q2$ = 0.239 (2) Å and the spherical polar angle $\varphi2$ = 137.2 (5)° (Cremer & Pople, 1975). The benzothiophene system is nearly perpendicular to the mean plane through the isoxazoline ring (N1/O1/C8–C10) and to the C11–C16 phenyl ring, as indicated by the dihedral angles of 86.10 (10) and 87.46 (11)°, respectively, between them. The dihedral angle between the fused ring system and the C17–C22 phenyl ring is 65.80 (11)°.

In the crystal, molecules are linked together by C9—H9···O1^{ii} and C19—H19···O2^{i} hydrogen bonds and by π–π interactions between inversion-related benzene rings of adjacent benzothiophene ring systems [intercentroid distance = 3.702 (2) Å] to form a three-dimensional network (Fig. 2 and Table 1).

Synthesis and crystallization

In a 100 ml flask, 2 mmol of (*Z*)-2-benzylidenebenzo[*b*]thio-]thiophen-3-one and 2.2 mmol of benzonitrile oxide were dissolved in 20 ml of chloroform. The mixture was cooled to 273 K under magnetic stirring in an ice bath. Then 15 ml of bleach (NaOCl, 24%) was added drop-by-drop without exceeding a temperature of 278 K. The mixture was left stirring for 4 h at room temperature, washed with water until the pH was neutral and dried over sodium sulfate (Na_2SO_4). The solvent was then removed under reduced pressure and the resulting residue was crystallized from ethanol (yield: 90%; m.p. 495 K). Colourless block-like crystals were obtained by slow evaporation of the ethanolic solution.

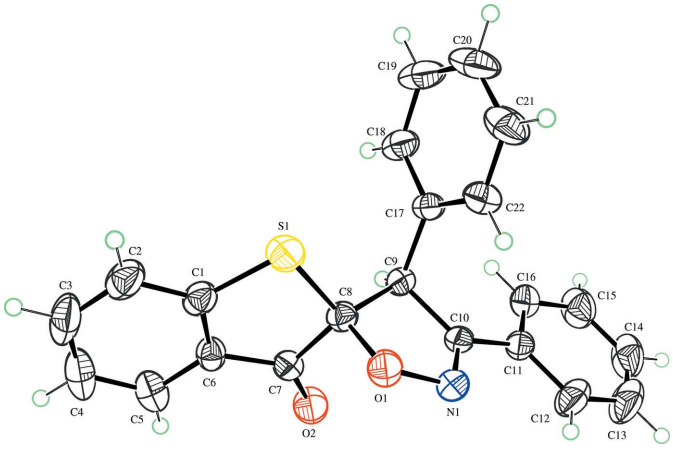


Figure 1
A plot of the molecule of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small circles.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{15}NO_2S$
M_r	357.41
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, *b*, *c* (Å)	9.2650 (2), 10.3523 (2), 36.0698 (8)
V (Å^3)	3459.60 (13)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.20
Crystal size (mm)	0.35 × 0.28 × 0.25
Data collection	
Diffractometer	Bruker X8 APEX
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.639, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	76407, 3811, 2597
R_{int}	0.089
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.105, 1.06
No. of reflections	3811
No. of parameters	235
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, −0.26

Computer programs: *APEX2* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS2016* (Sheldrick, 2015*a*), *SHELXL2016* (Sheldrick, 2015*b*), *ORTEP-3* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

The authors thank the Unit of Support for Technical and Scientific Research (UATRS, CNRST) for the X-ray measurements.

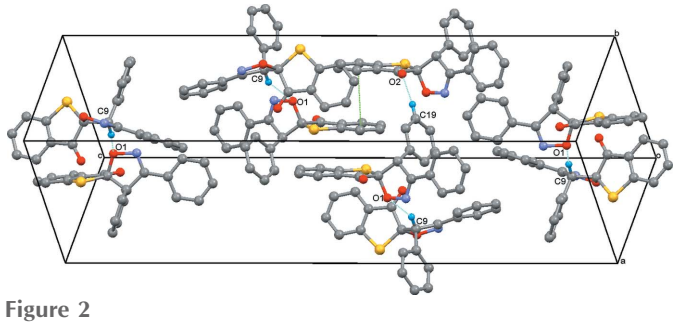


Figure 2
Crystal packing for the title compound showing molecules linked by hydrogen bonds (dashed blue lines) and a π–π interaction (green line).

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full crystallographic data

IUCrData (2018). **3**, x181019 [https://doi.org/10.1107/S2414314618010192]

3′,4′-Diphenyl-3*H*,4′*H*-spiro[benzo[*b*]thiophene-2,5′-isoxazol]-3-one

Mohamed Bakhouch, Mohamed El Yazidi, Ghali Al Houari, Mohamed Saadi and Lahcen El Ammari

3′,4′-Diphenyl-3*H*,4′*H*-spiro[benzo[*b*]thiophene-2,5′-isoxazol]-3-one

Crystal data

$C_{22}H_{15}NO_2S$
M_r = 357.41
Orthorhombic, *Pbca*
a = 9.2650 (2) Å
b = 10.3523 (2) Å
c = 36.0698 (8) Å
V = 3459.60 (13) Å^3
Z = 8
$F(000)$ = 1488
D_x = 1.372 Mg m^{-3}
Melting point: 495 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3811 reflections
θ = 3.0–27.1°
μ = 0.20 mm^{-1}
T = 296 K
Block, colourless
0.35 × 0.28 × 0.25 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.639, T_{max} = 0.747
76407 measured reflections
3811 independent reflections
2597 reflections with $I > 2\sigma(I)$
R_{int} = 0.089
θ_{max} = 27.1°, θ_{min} = 3.0°
h = −11→11
k = −13→13
l = −46→46

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.105
S = 1.06
3811 reflections
235 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 2.5234P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2409 (3)	0.4525 (2)	0.52031 (6)	0.0450 (5)
C2	0.2733 (3)	0.4617 (3)	0.48281 (7)	0.0620 (7)
H2	0.351287	0.510587	0.474656	0.074*
C3	0.1865 (4)	0.3962 (3)	0.45792 (7)	0.0750 (9)
H3	0.207713	0.400469	0.432749	0.090*
C4	0.0696 (4)	0.3248 (3)	0.46947 (7)	0.0739 (9)
H4	0.012838	0.282128	0.452088	0.089*
C5	0.0360 (3)	0.3160 (2)	0.50654 (7)	0.0559 (7)
H5	−0.043069	0.268137	0.514492	0.067*
C6	0.1239 (2)	0.3807 (2)	0.53187 (6)	0.0399 (5)
C7	0.1038 (2)	0.3808 (2)	0.57209 (6)	0.0386 (5)
C8	0.2164 (2)	0.4696 (2)	0.59144 (6)	0.0372 (5)
C9	0.2811 (2)	0.40827 (19)	0.62647 (5)	0.0338 (4)
H9	0.274619	0.313886	0.625187	0.041*
C10	0.1760 (2)	0.4606 (2)	0.65481 (6)	0.0361 (5)
C11	0.1605 (2)	0.4157 (2)	0.69323 (6)	0.0414 (5)
C12	0.0655 (3)	0.4780 (3)	0.71734 (7)	0.0623 (7)
H12	0.010973	0.547609	0.708966	0.075*
C13	0.0521 (4)	0.4369 (3)	0.75341 (8)	0.0802 (10)
H13	−0.010154	0.480009	0.769415	0.096*
C14	0.1291 (4)	0.3337 (3)	0.76594 (8)	0.0788 (10)
H14	0.118796	0.306354	0.790355	0.095*
C15	0.2214 (3)	0.2704 (3)	0.74268 (7)	0.0706 (8)
H15	0.273459	0.199575	0.751241	0.085*
C16	0.2378 (3)	0.3114 (2)	0.70626 (6)	0.0519 (6)
H16	0.301303	0.268334	0.690577	0.062*
C17	0.4353 (2)	0.4498 (2)	0.63469 (6)	0.0370 (5)
C22	0.4642 (2)	0.5692 (2)	0.65033 (7)	0.0491 (6)
H22	0.388181	0.622907	0.657125	0.059*
C21	0.6048 (3)	0.6096 (3)	0.65596 (8)	0.0665 (8)
H21	0.623101	0.689521	0.666765	0.080*
C20	0.7171 (3)	0.5314 (3)	0.64558 (8)	0.0731 (9)
H20	0.811760	0.558786	0.649034	0.088*
C19	0.6900 (3)	0.4130 (3)	0.63010 (8)	0.0670 (8)
H19	0.766504	0.360381	0.623001	0.080*
C18	0.5501 (2)	0.3713 (3)	0.62498 (7)	0.0506 (6)
H18	0.532736	0.290003	0.614950	0.061*
N1	0.1012 (2)	0.55663 (18)	0.64309 (5)	0.0452 (5)
O1	0.13553 (17)	0.58038 (14)	0.60528 (4)	0.0479 (4)
O2	0.01376 (18)	0.32410 (17)	0.58958 (4)	0.0573 (5)
S1	0.34013 (7)	0.52549 (7)	0.55640 (2)	0.05418 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0463 (12)	0.0488 (13)	0.0398 (12)	0.0096 (11)	0.0056 (11)	0.0066 (10)
C2	0.0635 (17)	0.0751 (18)	0.0475 (14)	0.0168 (15)	0.0149 (13)	0.0167 (14)
C3	0.111 (3)	0.081 (2)	0.0328 (13)	0.029 (2)	0.0067 (16)	0.0039 (14)
C4	0.114 (3)	0.0680 (18)	0.0396 (14)	0.0096 (19)	−0.0178 (17)	−0.0058 (13)
C5	0.0714 (18)	0.0473 (14)	0.0489 (14)	−0.0008 (13)	−0.0141 (13)	−0.0007 (11)
C6	0.0481 (13)	0.0367 (11)	0.0350 (11)	0.0038 (10)	−0.0022 (10)	0.0007 (9)
C7	0.0374 (11)	0.0405 (12)	0.0379 (11)	0.0005 (10)	−0.0016 (10)	0.0003 (9)
C8	0.0348 (11)	0.0393 (11)	0.0376 (11)	−0.0020 (9)	0.0025 (9)	−0.0007 (9)
C9	0.0326 (10)	0.0323 (10)	0.0366 (11)	0.0000 (9)	0.0026 (9)	−0.0011 (9)
C10	0.0280 (10)	0.0414 (12)	0.0388 (11)	−0.0031 (9)	0.0007 (9)	−0.0058 (9)
C11	0.0347 (11)	0.0504 (13)	0.0390 (12)	−0.0098 (10)	0.0047 (10)	−0.0072 (10)
C12	0.0607 (16)	0.0700 (17)	0.0562 (15)	−0.0021 (14)	0.0218 (13)	−0.0079 (13)
C13	0.089 (2)	0.096 (2)	0.0560 (18)	−0.016 (2)	0.0363 (17)	−0.0151 (17)
C14	0.093 (2)	0.104 (3)	0.0394 (15)	−0.031 (2)	0.0116 (16)	0.0003 (16)
C15	0.080 (2)	0.084 (2)	0.0477 (15)	−0.0050 (17)	−0.0041 (15)	0.0108 (14)
C16	0.0511 (14)	0.0647 (16)	0.0398 (12)	−0.0006 (12)	0.0003 (12)	−0.0028 (11)
C17	0.0301 (10)	0.0436 (12)	0.0371 (11)	0.0017 (9)	0.0014 (9)	0.0076 (9)
C22	0.0386 (12)	0.0511 (14)	0.0577 (15)	−0.0033 (11)	−0.0040 (11)	0.0001 (11)
C21	0.0526 (16)	0.0736 (18)	0.0733 (19)	−0.0251 (15)	−0.0138 (15)	0.0095 (15)
C20	0.0347 (14)	0.106 (3)	0.078 (2)	−0.0182 (16)	−0.0103 (14)	0.0378 (19)
C19	0.0351 (13)	0.094 (2)	0.0723 (19)	0.0148 (14)	0.0112 (13)	0.0296 (17)
C18	0.0408 (12)	0.0587 (15)	0.0522 (14)	0.0094 (11)	0.0071 (11)	0.0090 (12)
N1	0.0402 (10)	0.0518 (12)	0.0435 (11)	0.0055 (9)	0.0003 (9)	−0.0080 (9)
O1	0.0543 (10)	0.0428 (9)	0.0467 (9)	0.0107 (7)	−0.0041 (8)	−0.0014 (7)
O2	0.0514 (10)	0.0706 (11)	0.0499 (10)	−0.0228 (9)	0.0048 (8)	0.0013 (9)
S1	0.0460 (3)	0.0679 (4)	0.0486 (3)	−0.0160 (3)	0.0036 (3)	0.0130 (3)

Geometric parameters (Å, º)

C1—C6	1.379 (3)	C11—C12	1.396 (3)
C1—C2	1.389 (3)	C12—C13	1.374 (4)
C1—S1	1.763 (2)	C12—H12	0.9300
C2—C3	1.383 (4)	C13—C14	1.362 (4)
C2—H2	0.9300	C13—H13	0.9300
C3—C4	1.376 (4)	C14—C15	1.366 (4)
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.376 (4)	C15—C16	1.389 (3)
C4—H4	0.9300	C15—H15	0.9300
C5—C6	1.395 (3)	C16—H16	0.9300
C5—H5	0.9300	C17—C18	1.383 (3)
C6—C7	1.463 (3)	C17—C22	1.385 (3)
C7—O2	1.199 (2)	C22—C21	1.383 (3)
C7—C8	1.555 (3)	C22—H22	0.9300
C8—O1	1.459 (2)	C21—C20	1.370 (4)
C8—C9	1.536 (3)	C21—H21	0.9300

C8—S1	1.802 (2)	C20—C19	1.371 (4)
C9—C10	1.512 (3)	C20—H20	0.9300
C9—C17	1.521 (3)	C19—C18	1.379 (4)
C9—H9	0.9800	C19—H19	0.9300
C10—N1	1.283 (3)	C18—H18	0.9300
C10—C11	1.469 (3)	N1—O1	1.421 (2)
C11—C16	1.378 (3)		

C6—C1—C2	120.1 (2)	C12—C11—C10	120.2 (2)
C6—C1—S1	114.68 (16)	C13—C12—C11	120.2 (3)
C2—C1—S1	125.2 (2)	C13—C12—H12	119.9
C3—C2—C1	118.2 (3)	C11—C12—H12	119.9
C3—C2—H2	120.9	C14—C13—C12	120.7 (3)
C1—C2—H2	120.9	C14—C13—H13	119.7
C4—C3—C2	121.6 (2)	C12—C13—H13	119.7
C4—C3—H3	119.2	C13—C14—C15	120.1 (3)
C2—C3—H3	119.2	C13—C14—H14	120.0
C5—C4—C3	120.5 (3)	C15—C14—H14	120.0
C5—C4—H4	119.7	C14—C15—C16	120.2 (3)
C3—C4—H4	119.7	C14—C15—H15	119.9
C4—C5—C6	118.2 (3)	C16—C15—H15	119.9
C4—C5—H5	120.9	C11—C16—C15	120.4 (2)
C6—C5—H5	120.9	C11—C16—H16	119.8
C1—C6—C5	121.3 (2)	C15—C16—H16	119.8
C1—C6—C7	113.6 (2)	C18—C17—C22	118.6 (2)
C5—C6—C7	125.2 (2)	C18—C17—C9	120.4 (2)
O2—C7—C6	127.6 (2)	C22—C17—C9	120.90 (19)
O2—C7—C8	121.32 (19)	C21—C22—C17	120.8 (2)
C6—C7—C8	111.10 (18)	C21—C22—H22	119.6
O1—C8—C9	104.11 (15)	C17—C22—H22	119.6
O1—C8—C7	105.87 (16)	C20—C21—C22	119.8 (3)
C9—C8—C7	112.77 (16)	C20—C21—H21	120.1
O1—C8—S1	108.32 (13)	C22—C21—H21	120.1
C9—C8—S1	117.48 (14)	C21—C20—C19	120.0 (2)
C7—C8—S1	107.57 (14)	C21—C20—H20	120.0
C10—C9—C17	111.83 (16)	C19—C20—H20	120.0
C10—C9—C8	99.02 (16)	C20—C19—C18	120.5 (3)
C17—C9—C8	114.22 (16)	C20—C19—H19	119.8
C10—C9—H9	110.4	C18—C19—H19	119.8
C17—C9—H9	110.4	C19—C18—C17	120.3 (3)
C8—C9—H9	110.4	C19—C18—H18	119.8
N1—C10—C11	120.21 (19)	C17—C18—H18	119.8
N1—C10—C9	113.72 (18)	C10—N1—O1	109.23 (16)
C11—C10—C9	125.98 (19)	N1—O1—C8	107.90 (14)
C16—C11—C12	118.5 (2)	C1—S1—C8	92.77 (10)
C16—C11—C10	121.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19···O2^{i}	0.93	2.62	3.462 (3)	152
C9—H9···O1^{ii}	0.98	2.66	3.564 (2)	154

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1/2, y-1/2, z$.