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3′-(4-Chlorophenyl)-4′-phenyl-3*H*,4′*H*-spiro[benzo-[*b*]thiophene-2,5′-isoxazol]-3-one

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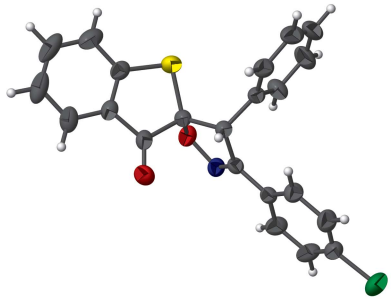
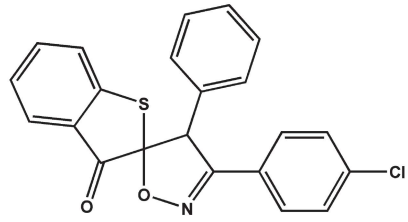
The molecule of the title compound, $C_{22}H_{14}ClNO_2S$, is built up from an isoxazole ring linked to a benzothiophene ring system with additional phenyl and 4-chlorophenyl substituents. The benzothiophene system is virtually planar with the largest deviation from the mean plane being 0.041 (2) Å, while the isoxazole ring adopts an envelope conformation. The plane of the benzothiophene ring system is almost perpendicular to those of the phenyl and the 4-chlorophenyl rings, with dihedral angles of 64.76 (10) and 82.81 (10)°, respectively, between them. The phenyl ring is inclined by 85.76 (12)° to the plane of the 4-chlorophenyl ring, which in turn lies close to the plane of the isoxazole ring. In the crystal, molecules are linked by weak C—H···O hydrogen bonds and offset π–π interactions between the aromatic rings of adjacent benzothiophene ring systems. These combine to form a three-dimensional network structure.

3D view



Chemical scheme



Structure description

Spiro-isoxazolines exhibit a wide range of applications in many fields (Al Houari *et al.*, 2008; Hwang *et al.*, 2005). Furthermore, they act as suitable precursors to a number of molecules with biological activities (Bode & Carreira, 2001; Tang *et al.*, 2010). The 1,3-dipolar cycloaddition reaction of nitrile oxides to olefins is an efficient synthetic route to these heterocyclic systems in a one-pot reaction. In an extension of work in this area by our group (Bakhouch *et al.*, 2014; Boughaleb *et al.*, 2011), we have investigated the 1,3-dipolar cycloaddition reaction of nitrile oxides with thioaurones as the dipolarophile with an exocyclic double bond in order to determine if there were selectivity problems with cycloaddition reaction. We report herein the 1,3-dipolar cycloaddition reaction

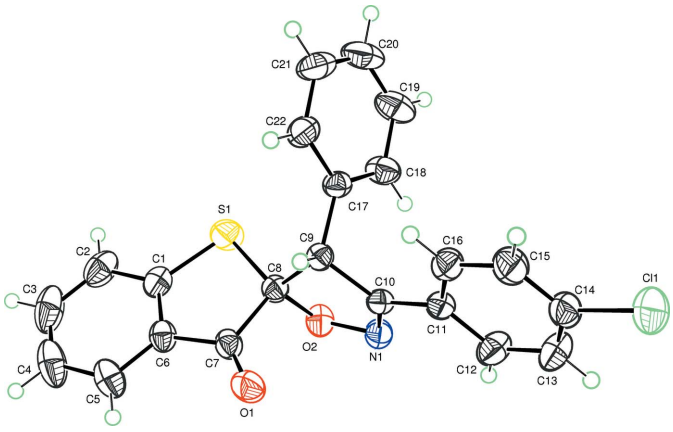


Figure 1
The molecule of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

between *p*-chlorobenzonitriloxide and (*Z*)-2-benzylidenebenzo[*b*]thiophen-3-one. The reaction is regiospecific and leads only to a single regioisomer as a racemic adduct. This regiospecifity was established by spectroscopic analysis IR, ^{1}H NMR and ^{13}C NMR and confirmed by the X-ray study.

In the title compound, the fused five- and six-membered benzothiophene ring system is almost planar with the maximum deviation from the mean plane being 0.041 (2) Å at C8. The plane of this ring system makes dihedral angles of 64.76 (10) and 82.81 (10)°, respectively, with the planes through the phenyl and the 4-chlorophenyl rings (Fig. 1). The isoxazole ring (N1/O2/C8–C10) adopts an envelope conformation with atom C8 as the flap, as indicated by the total puckering amplitude Q_2 = 0.2377 (19) Å, and spherical polar angle φ_2 = 316.8 (5)°. The dihedral angle between the mean plane of the phenyl ring and that of the 4-chlorophenyl group is 85.76 (12)°.

In the crystal, molecules are linked by weak C9—H9···O2 hydrogen bonds (Table 1) and π–π interactions between the C1–C6 benzene rings of the benzothiophene ring system [intercentroid distance 3.697 (2) Å], forming a three-dimensional network as shown in Fig. 2.

Synthesis and crystallization

In a 100 ml flask, 2 mmol of (*Z*)-2-benzylidenebenzo[*b*]thiophen-3-one and 2.2 mmol of *p*-chlorobenzonitriloxide 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° Chl) was added dropwise without exceeding a temperature of 278 K. The mixture was left under magnetic stirring for 4 h at room temperature, washed with water until neutral pH and dried over sodium sulfate (Na_2SO_4). The solvent was then removed under reduced pressure and the resulting residue was crystallized by slow evaporation from ethanol solution (yield: 85%; m.p.: 475 K) giving colourless block-like.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O2^{i}	0.98	2.66	3.574 (2)	155

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{14}ClNO_2S$
M_r	391.85
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, *b*, *c* (Å)	9.2518 (2), 10.3432 (2), 38.5674 (7)
V (Å^3)	3690.64 (13)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.34
Crystal size (mm)	0.36 × 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	70305, 4400, 3106
R_{int}	0.074
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.128, 1.02
No. of reflections	4400
No. of parameters	244
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (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.

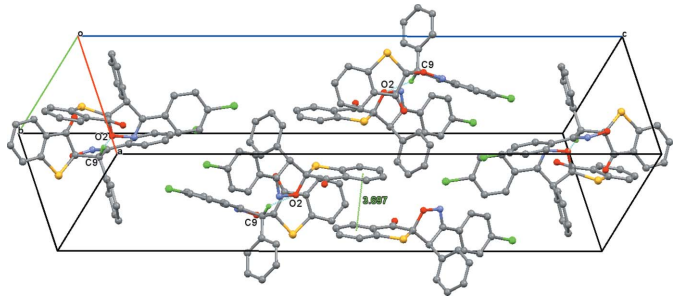


Figure 2
Crystal packing for the title compound, showing molecules linked by hydrogen bonds (blue dashed lines) and π–π interactions (green lines).

References

Al Houari, G., Kerbal, A., Bennani, B., Baba, M. F., Daoudi, M. & Ben Hadda, T. (2008). *ARKIVOC*, **xii**, 42–50.

Bakhouch, M., Al Houari, G., El Yazidi, M., Saadi, M. & El Ammari, L. (2014). *Acta Cryst.* E**70**, o587.

Bode, J. W. & Carreira, E. M. (2001). *Org. Lett.* **3**, 1587–1590.

Boughaleb, A., Zouihri, H., Gmouh, S., Kerbal, A. & El yazidi, M. (2011). *Acta Cryst.* E**67**, o1850.

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Hwang, I. T., Kim, H. R., Jeon, D. J., Hong, K. S., Song, J. H. & Cho, K. Y. (2005). *J. Agric. Food Chem.* **53**, 8639–8643.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Tang, S., He, J., Sun, Y., He, L. & She, X. (2010). *J. Org. Chem.* **75**, 1961–1966.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2017). **2**, x170677 [https://doi.org/10.1107/S2414314617006770]

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Crystal data

$C_{22}H_{14}ClNO_2S$
M_r = 391.85
Orthorhombic, *Pbca*
a = 9.2518 (2) Å
b = 10.3432 (2) Å
c = 38.5674 (7) Å
V = 3690.64 (13) Å^3
Z = 8
$F(000)$ = 1616
D_x = 1.410 Mg m^{-3}
Melting point: 475 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4400 reflections
θ = 3.0–27.9°
μ = 0.34 mm^{-1}
T = 296 K
Block, colourless
0.36 × 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
70305 measured reflections
4400 independent reflections
3106 reflections with $I > 2\sigma(I)$
R_{int} = 0.074
θ_{max} = 27.9°, θ_{min} = 3.0°
h = −12→12
k = −13→13
l = −50→49

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.128
S = 1.02
4400 reflections
244 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 2.1391P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 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	0.2379 (2)	0.5465 (2)	0.51932 (5)	0.0419 (5)
C2	0.2730 (3)	0.5365 (3)	0.48431 (6)	0.0593 (7)
H2	0.3507	0.4865	0.4770	0.071*
C3	0.1886 (4)	0.6036 (3)	0.46081 (7)	0.0736 (9)
H3	0.2114	0.5992	0.4374	0.088*
C4	0.0723 (4)	0.6764 (3)	0.47105 (7)	0.0706 (8)
H4	0.0175	0.7199	0.4546	0.085*
C5	0.0364 (3)	0.6854 (2)	0.50560 (6)	0.0531 (6)
H5	−0.0428	0.7341	0.5127	0.064*
C6	0.1210 (2)	0.6202 (2)	0.52966 (5)	0.0381 (5)
C7	0.0987 (2)	0.6213 (2)	0.56734 (5)	0.0374 (4)
C8	0.2113 (2)	0.53115 (19)	0.58570 (5)	0.0343 (4)
C9	0.27888 (19)	0.59366 (19)	0.61807 (5)	0.0316 (4)
H9	0.2734	0.6881	0.6165	0.038*
C10	0.17414 (19)	0.54358 (19)	0.64512 (5)	0.0324 (4)
C11	0.1640 (2)	0.58866 (19)	0.68110 (5)	0.0345 (4)
C12	0.0650 (2)	0.5337 (2)	0.70385 (6)	0.0498 (6)
H12	0.0018	0.4705	0.6958	0.060*
C13	0.0587 (3)	0.5714 (3)	0.73808 (6)	0.0565 (6)
H13	−0.0069	0.5330	0.7532	0.068*
C14	0.1505 (2)	0.6663 (2)	0.74963 (6)	0.0478 (5)
C15	0.2466 (3)	0.7254 (3)	0.72761 (6)	0.0513 (6)
H15	0.3063	0.7913	0.7356	0.062*
C16	0.2536 (2)	0.6858 (2)	0.69323 (6)	0.0437 (5)
H16	0.3190	0.7249	0.6782	0.052*
C17	0.4330 (2)	0.5510 (2)	0.62577 (5)	0.0345 (4)
C18	0.4601 (2)	0.4323 (2)	0.64096 (7)	0.0483 (6)
H18	0.3835	0.3799	0.6477	0.058*
C19	0.6009 (3)	0.3912 (3)	0.64614 (8)	0.0638 (7)
H19	0.6184	0.3114	0.6565	0.077*
C20	0.7146 (3)	0.4674 (3)	0.63614 (7)	0.0644 (8)
H20	0.8090	0.4391	0.6395	0.077*
C21	0.6887 (2)	0.5858 (3)	0.62118 (7)	0.0594 (7)
H21	0.7658	0.6376	0.6144	0.071*
C22	0.5481 (2)	0.6283 (2)	0.61618 (6)	0.0452 (5)
H22	0.5313	0.7091	0.6064	0.054*
N1	0.09749 (19)	0.44767 (17)	0.63487 (4)	0.0400 (4)
O1	0.01108 (18)	0.67623 (17)	0.58298 (4)	0.0557 (4)
O2	0.12943 (16)	0.42202 (14)	0.59942 (4)	0.0427 (4)
Cl1	0.14661 (9)	0.71124 (9)	0.79305 (2)	0.0767 (3)
S1	0.33513 (7)	0.47121 (7)	0.55304 (2)	0.05245 (18)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0456 (11)	0.0433 (12)	0.0368 (10)	−0.0099 (10)	0.0034 (9)	−0.0048 (9)
C2	0.0639 (16)	0.0671 (17)	0.0468 (14)	−0.0162 (14)	0.0149 (12)	−0.0139 (13)
C3	0.112 (3)	0.078 (2)	0.0310 (12)	−0.0293 (19)	0.0042 (15)	−0.0040 (13)
C4	0.110 (2)	0.0641 (17)	0.0381 (13)	−0.0108 (18)	−0.0218 (15)	0.0061 (13)
C5	0.0694 (16)	0.0451 (13)	0.0450 (13)	0.0001 (12)	−0.0160 (12)	0.0007 (11)
C6	0.0469 (11)	0.0354 (10)	0.0320 (10)	−0.0044 (9)	−0.0028 (9)	−0.0005 (8)
C7	0.0396 (10)	0.0391 (11)	0.0336 (10)	−0.0051 (9)	−0.0048 (9)	0.0020 (9)
C8	0.0345 (10)	0.0349 (10)	0.0334 (10)	0.0016 (8)	0.0001 (8)	0.0010 (8)
C9	0.0326 (9)	0.0295 (10)	0.0327 (9)	−0.0009 (8)	0.0000 (8)	0.0007 (8)
C10	0.0277 (9)	0.0352 (10)	0.0344 (10)	−0.0007 (8)	−0.0010 (7)	0.0027 (8)
C11	0.0317 (9)	0.0364 (10)	0.0353 (10)	0.0025 (8)	0.0000 (8)	0.0027 (8)
C12	0.0462 (12)	0.0541 (14)	0.0492 (13)	−0.0101 (11)	0.0104 (10)	−0.0043 (11)
C13	0.0591 (14)	0.0650 (16)	0.0454 (13)	−0.0045 (13)	0.0185 (11)	−0.0004 (12)
C14	0.0493 (12)	0.0584 (14)	0.0358 (11)	0.0122 (11)	0.0014 (10)	−0.0027 (11)
C15	0.0522 (13)	0.0583 (15)	0.0434 (12)	−0.0070 (11)	−0.0060 (11)	−0.0059 (11)
C16	0.0416 (11)	0.0502 (13)	0.0394 (11)	−0.0067 (10)	0.0014 (10)	0.0010 (10)
C17	0.0304 (9)	0.0387 (11)	0.0343 (10)	−0.0017 (8)	0.0005 (8)	−0.0050 (8)
C18	0.0380 (11)	0.0448 (13)	0.0620 (15)	0.0028 (10)	−0.0055 (10)	0.0048 (11)
C19	0.0500 (14)	0.0637 (17)	0.0775 (19)	0.0191 (13)	−0.0159 (13)	−0.0027 (14)
C20	0.0346 (12)	0.093 (2)	0.0660 (17)	0.0149 (14)	−0.0103 (11)	−0.0278 (16)
C21	0.0344 (11)	0.088 (2)	0.0561 (15)	−0.0131 (12)	0.0079 (10)	−0.0206 (14)
C22	0.0400 (11)	0.0548 (14)	0.0409 (12)	−0.0076 (10)	0.0048 (9)	−0.0033 (10)
N1	0.0397 (9)	0.0443 (10)	0.0359 (9)	−0.0052 (8)	−0.0012 (7)	0.0032 (8)
O1	0.0493 (9)	0.0667 (11)	0.0510 (10)	0.0194 (8)	−0.0012 (8)	0.0049 (8)
O2	0.0510 (9)	0.0388 (8)	0.0383 (8)	−0.0096 (7)	−0.0036 (7)	−0.0007 (6)
Cl1	0.0799 (5)	0.1115 (7)	0.0388 (3)	0.0083 (4)	0.0024 (3)	−0.0163 (4)
S1	0.0477 (3)	0.0635 (4)	0.0462 (3)	0.0151 (3)	0.0033 (3)	−0.0106 (3)

Geometric parameters (Å, º)

C1—C6	1.382 (3)	C11—C12	1.390 (3)
C1—C2	1.393 (3)	C12—C13	1.378 (3)
C1—S1	1.763 (2)	C12—H12	0.9300
C2—C3	1.383 (4)	C13—C14	1.372 (4)
C2—H2	0.9300	C13—H13	0.9300
C3—C4	1.371 (5)	C14—C15	1.373 (3)
C3—H3	0.9300	C14—Cl1	1.738 (2)
C4—C5	1.376 (4)	C15—C16	1.390 (3)
C4—H4	0.9300	C15—H15	0.9300
C5—C6	1.389 (3)	C16—H16	0.9300
C5—H5	0.9300	C17—C22	1.383 (3)
C6—C7	1.468 (3)	C17—C18	1.383 (3)
C7—O1	1.160 (3)	C18—C19	1.385 (3)
C7—C8	1.567 (3)	C18—H18	0.9300
C8—O2	1.458 (2)	C19—C20	1.369 (4)

C8—C9	1.539 (3)	C19—H19	0.9300
C8—S1	1.812 (2)	C20—C21	1.375 (4)
C9—C10	1.515 (3)	C20—H20	0.9300
C9—C17	1.521 (3)	C21—C22	1.386 (3)
C9—H9	0.9800	C21—H21	0.9300
C10—N1	1.282 (3)	C22—H22	0.9300
C10—C11	1.467 (3)	N1—O2	1.424 (2)
C11—C16	1.383 (3)		

C6—C1—C2	120.2 (2)	C12—C11—C10	120.59 (19)
C6—C1—S1	115.48 (16)	C13—C12—C11	121.1 (2)
C2—C1—S1	124.3 (2)	C13—C12—H12	119.4
C3—C2—C1	117.8 (3)	C11—C12—H12	119.4
C3—C2—H2	121.1	C14—C13—C12	119.2 (2)
C1—C2—H2	121.1	C14—C13—H13	120.4
C4—C3—C2	122.0 (2)	C12—C13—H13	120.4
C4—C3—H3	119.0	C13—C14—C15	121.2 (2)
C2—C3—H3	119.0	C13—C14—Cl1	119.41 (19)
C3—C4—C5	120.4 (3)	C15—C14—Cl1	119.37 (19)
C3—C4—H4	119.8	C14—C15—C16	119.3 (2)
C5—C4—H4	119.8	C14—C15—H15	120.4
C4—C5—C6	118.5 (3)	C16—C15—H15	120.4
C4—C5—H5	120.7	C11—C16—C15	120.6 (2)
C6—C5—H5	120.7	C11—C16—H16	119.7
C1—C6—C5	121.1 (2)	C15—C16—H16	119.7
C1—C6—C7	113.57 (19)	C22—C17—C18	119.1 (2)
C5—C6—C7	125.3 (2)	C22—C17—C9	120.16 (19)
O1—C7—C6	128.1 (2)	C18—C17—C9	120.67 (18)
O1—C7—C8	121.42 (19)	C17—C18—C19	120.3 (2)
C6—C7—C8	110.47 (18)	C17—C18—H18	119.8
O2—C8—C9	104.00 (15)	C19—C18—H18	119.8
O2—C8—C7	106.23 (15)	C20—C19—C18	120.3 (3)
C9—C8—C7	112.77 (16)	C20—C19—H19	119.8
O2—C8—S1	108.40 (13)	C18—C19—H19	119.8
C9—C8—S1	116.78 (13)	C19—C20—C21	119.8 (2)
C7—C8—S1	108.03 (13)	C19—C20—H20	120.1
C10—C9—C17	111.45 (15)	C21—C20—H20	120.1
C10—C9—C8	98.91 (15)	C20—C21—C22	120.3 (2)
C17—C9—C8	114.68 (16)	C20—C21—H21	119.9
C10—C9—H9	110.4	C22—C21—H21	119.9
C17—C9—H9	110.4	C17—C22—C21	120.2 (2)
C8—C9—H9	110.4	C17—C22—H22	119.9
N1—C10—C11	120.17 (18)	C21—C22—H22	119.9
N1—C10—C9	113.95 (17)	C10—N1—O2	109.00 (16)
C11—C10—C9	125.69 (17)	N1—O2—C8	108.18 (14)
C16—C11—C12	118.6 (2)	C1—S1—C8	92.23 (10)
C16—C11—C10	120.84 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O2^{i}	0.98	2.66	3.574 (2)	155

Symmetry code: (i) −*x*+1/2, *y*+1/2, *z*.