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(7*RS*,8*SR*)-Ethyl 6-(1,3-benzodioxol-5-yl)-3-(3-bromo-2-thienyl)-2-oxocyclohex-3-ene-1-carboxylate

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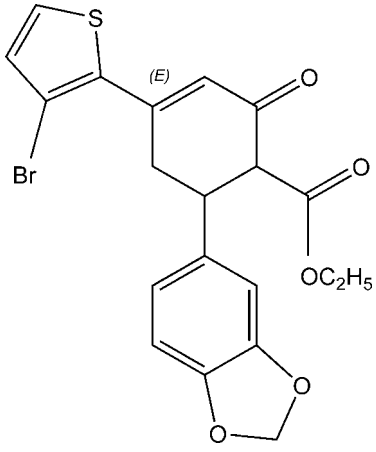
Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.006 Å; R factor = 0.052; wR factor = 0.117; data-to-parameter ratio = 14.4.

The title compound, $C_{20}H_{17}BrO_5S$, crystallizes as a racemate. The dihedral angle between the thiophene and benzene rings is 66.91 (13)°.

Related literature

For related literature, see: Dhar (1981); Dimmock *et al.* (1999); House (1972); Padmavathi *et al.* (1999, 2000); Padmavathi, Sharmila, Balaiah *et al.* (2001); Padmavathi, Sharmila, Somashekara Reddy & Bhaskar Reddy (2001); Tabba *et al.* (1995).



Experimental

Crystal data

$C_{20}H_{17}BrO_5S$
M_r = 449.32
Monoclinic, $P2_1/c$
a = 17.3207 (12) Å
b = 11.8106 (9) Å
c = 9.3661 (8) Å
β = 97.736 (7)°
V = 1898.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.30 mm^{-1}
T = 299 K
0.35 × 0.30 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: numerical (Herrendorf & Bärnighausen, 1997)
T_{min} = 0.593, T_{max} = 0.851
17735 measured reflections
3518 independent reflections
2325 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.118
S = 1.11
3518 reflections
244 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2022).

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supplementary materials

Acta Cryst. (2007). E**63**, o3616 [**doi:10.1107/S1600536807035106**]

(7*RS*,8*SR*)-Ethyl 6-(1,3-benzodioxol-5-yl)-3-(3-bromo-2-thienyl)-2-oxocyclohex-3-ene-1-carboxylate

A. Fischer, H. S. Yathirajan, B. V. Ashalatha, B. Narayana and B. K. Sarojini

Comment

Chalcones and the corresponding heterocyclic analogues are valuable intermediates in organic synthesis (Dhar, 1981) and exhibit a multitude of biological activities (Dimmock *et al.*, 1999). An important feature of chalcones and their heteroanalogues is their ability to act as activated unsaturated systems in conjugated addition reactions of carbanions in the presence of basic catalysts (House, 1972). This type of reaction may be exploited for obtaining highly functionalized cyclohexene derivatives (Tabba *et al.*, 1995), but is more commonly used for the preparation of 3,5-diaryl-6-carbethoxycyclohexanones *via* Michael addition of ethyl acetoacetate. The mentioned cyclohexenones are efficient synthons in building spiro compounds (Padmavathi, Sharmila, Somashekara Reddy *et al.*, 2001) or as intermediates in the synthesis of benzisoxazoles or carbazole derivatives (Padmavathi *et al.*, 1999; 2000, Padmavathi, Sharmila, Balaiah *et al.*, 2001). In view of the importance of these derivatives, the title compound was synthesized and crystallized and the structure was determined.

The compound is prepared by the cyclocondensation of ethyl acetoacetate with (2*E*)-3-(1,3-benzodioxol-5-yl)-1-(3-bromo-2-thienyl)prop-2-en-1-one, which leads to the generation of two chiral centers at C7 and C8. As the reaction is not stereoselective, both configurations of the chiral carbon atoms are expected to be obtained, which would result in a mixture of diastereomers. No attempts to separate the diastereomers were undertaken and the crystals were grown from the mixture after recrystallization.

The geometry of the molecule is unexceptional. The dihedral angle between the phenyl ring and the thiophene group is 66.91 (13)°.

Experimental

(2*E*)-3-(1,3-Benzodioxol-5-yl)-1-(3-bromo-2-thienyl)prop-2-en-1-one**(**1.69 g**,** 5 mmol) and ethyl acetoacetate (0.65 g, 5 mmol) were refluxed for 4hrs in 20 ml e thanol in presence of 0.8 ml 10% NaOH. The reaction mixture was cooled to room temperature and the reaction mass was filtered and recrystallized using methanol. Crystals were grown from acetone. (Yield: 61%; m.p.: 391–393 K). Analysis for $C_{20}H_{17}O_5SBr$: Found (Calculated): C: 53.34 (53.46%); H: 3.71 (3.81%); S: 7.09 (7.14%).

Refinement

Attempts to refine the structure using a disordered model for the ethoxy group did not yield satisfactory results. H atoms were placed at calculated positions and refined riding on the respective carrier atom (U_{iso}(H)=1.2 U_{eq} of the respective carrier atom (1.5 for the methyl group), d(C—H) 0.93 Å(aromatic/olefinic C), 0.96 Å (CH_3), 0.97 Å (CH_2), 0.98 Å (tertiary CH).

Figures

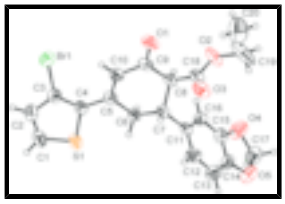


Fig. 1. : The molecular structure of the title compound. Displacement ellipsoids are drawn at the 40% probability level.

(7RS,8SR)-Ethyl 6-(1,3-benzodioxol-5-yl)-3-(3-bromo-2-thienyl)-2-oxocyclohex-3-ene-1-carboxylate

Crystal data

$C_{20}H_{17}BrO_5S$	F_{000} = 912
M_r = 449.32	D_x = 1.572 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 123 reflections
a = 17.3207 (12) Å	θ = 4.7–21.4º
b = 11.8106 (9) Å	μ = 2.30 mm^{-1}
c = 9.3661 (8) Å	T = 299 K
β = 97.736 (7)º	Plate, colourless
V = 1898.6 (3) Å^3	0.35 × 0.30 × 0.20 mm
Z = 4	

Data collection

Bruker–Nonius KappaCCD diffractometer	2325 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.062
φ & ω scans	θ_{max} = 25.5º
Absorption correction: numerical (Herrendorf & Bärnighausen, 1997)	θ_{min} = 4.6º
T_{min} = 0.593, T_{max} = 0.851	h = −20→20
17735 measured reflections	k = −14→14
3518 independent reflections	l = −11→11

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$w = 1/[\sigma^2(F_o^2) + (0.0317P)^2 + 2.7171P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.118	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.11	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
3518 reflections	$\Delta\rho_{min}$ = −0.47 e Å^{-3}
244 parameters	Extinction correction: none

Primary atom site location: structure-invariant direct methods

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 $F^2 > 2\sigma(F^2)$ 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}
Br1	0.41565 (3)	0.73085 (4)	0.98853 (6)	0.0749 (2)
S1	0.45442 (7)	0.47034 (12)	0.67283 (13)	0.0646 (4)
C1	0.3593 (3)	0.4947 (5)	0.6816 (5)	0.0695 (14)
H1	0.3189	0.4573	0.6251	0.083*
C2	0.3484 (3)	0.5738 (4)	0.7787 (5)	0.0617 (12)
H2	0.2996	0.5973	0.7981	0.074*
C3	0.4187 (2)	0.6175 (4)	0.8480 (4)	0.0499 (10)
C4	0.4839 (2)	0.5705 (3)	0.8045 (4)	0.0461 (10)
C5	0.5671 (2)	0.5879 (3)	0.8476 (4)	0.0433 (9)
C6	0.6226 (2)	0.5372 (4)	0.7523 (4)	0.0464 (10)
H6A	0.6277	0.5890	0.6738	0.056*
H6B	0.6006	0.4671	0.7109	0.056*
C7	0.7037 (2)	0.5131 (3)	0.8346 (4)	0.0432 (9)
H7	0.6972	0.4560	0.9081	0.052*
C8	0.7358 (2)	0.6195 (3)	0.9132 (4)	0.0455 (10)
H8	0.7445	0.6770	0.8416	0.055*
C9	0.6785 (3)	0.6662 (4)	1.0076 (4)	0.0536 (11)
C10	0.5963 (3)	0.6454 (4)	0.9659 (4)	0.0533 (11)
H10	0.5616	0.6736	1.0247	0.064*
C11	0.7569 (2)	0.4631 (3)	0.7358 (4)	0.0429 (9)
C12	0.7683 (3)	0.3478 (4)	0.7329 (5)	0.0636 (13)
H12	0.7440	0.3024	0.7948	0.076*
C13	0.8144 (3)	0.2966 (4)	0.6417 (6)	0.0769 (15)
H13	0.8203	0.2184	0.6394	0.092*
C14	0.8505 (3)	0.3653 (4)	0.5561 (5)	0.0589 (12)
C15	0.8405 (2)	0.4800 (4)	0.5584 (5)	0.0524 (11)
C16	0.7948 (2)	0.5316 (4)	0.6461 (5)	0.0518 (11)
H16	0.7891	0.6098	0.6462	0.062*
C17	0.9153 (4)	0.4379 (5)	0.3900 (6)	0.0843 (16)
H17A	0.8902	0.4358	0.2910	0.101*
H17B	0.9709	0.4474	0.3894	0.101*

C18	0.8121 (3)	0.5959 (4)	1.0062 (5)	0.0572 (12)
C19	0.9454 (5)	0.6571 (8)	1.0697 (8)	0.140 (3)
H19A	0.9557	0.5770	1.0852	0.169*
H19B	0.9842	0.6890	1.0157	0.169*
C20	0.9437 (5)	0.7139 (8)	1.1993 (10)	0.143 (3)
H20A	0.9317	0.7923	1.1803	0.215*
H20B	0.9936	0.7078	1.2572	0.215*
H20C	0.9046	0.6809	1.2499	0.215*
O1	0.7014 (2)	0.7217 (3)	1.1149 (4)	0.0782 (10)
O2	0.86292 (19)	0.6774 (3)	0.9936 (4)	0.0848 (11)
O3	0.8237 (2)	0.5135 (3)	1.0799 (4)	0.0757 (10)
O4	0.8855 (2)	0.5292 (3)	0.4645 (4)	0.0907 (12)
O5	0.9007 (2)	0.3362 (3)	0.4610 (4)	0.0807 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0724 (4)	0.0617 (3)	0.0943 (4)	0.0033 (3)	0.0245 (3)	−0.0144 (3)
S1	0.0488 (7)	0.0880 (9)	0.0555 (7)	−0.0104 (6)	0.0022 (5)	−0.0191 (7)
C1	0.047 (3)	0.092 (4)	0.066 (3)	−0.013 (3)	−0.003 (2)	−0.004 (3)
C2	0.048 (3)	0.072 (3)	0.066 (3)	0.002 (2)	0.010 (2)	0.014 (3)
C3	0.050 (3)	0.048 (3)	0.052 (2)	−0.001 (2)	0.010 (2)	0.010 (2)
C4	0.043 (2)	0.050 (2)	0.045 (2)	−0.005 (2)	0.0039 (18)	0.008 (2)
C5	0.049 (2)	0.044 (2)	0.038 (2)	−0.0057 (19)	0.0074 (18)	0.0036 (19)
C6	0.043 (2)	0.050 (3)	0.045 (2)	−0.0074 (19)	0.0019 (18)	−0.007 (2)
C7	0.044 (2)	0.043 (2)	0.042 (2)	−0.0074 (18)	0.0034 (17)	0.0012 (18)
C8	0.046 (2)	0.044 (2)	0.044 (2)	−0.0114 (19)	−0.0023 (18)	0.0003 (19)
C9	0.065 (3)	0.047 (3)	0.047 (2)	−0.014 (2)	0.001 (2)	−0.006 (2)
C10	0.057 (3)	0.057 (3)	0.048 (2)	−0.006 (2)	0.013 (2)	−0.007 (2)
C11	0.036 (2)	0.048 (2)	0.043 (2)	−0.0083 (18)	−0.0022 (17)	−0.0015 (19)
C12	0.073 (3)	0.046 (3)	0.074 (3)	−0.004 (2)	0.016 (3)	0.004 (2)
C13	0.087 (4)	0.053 (3)	0.094 (4)	0.008 (3)	0.022 (3)	−0.001 (3)
C14	0.051 (3)	0.063 (3)	0.062 (3)	0.014 (2)	0.004 (2)	−0.004 (2)
C15	0.045 (2)	0.058 (3)	0.055 (3)	0.001 (2)	0.007 (2)	0.009 (2)
C16	0.053 (3)	0.041 (2)	0.060 (3)	0.004 (2)	0.008 (2)	0.000 (2)
C17	0.083 (4)	0.096 (5)	0.077 (4)	0.018 (3)	0.022 (3)	−0.007 (3)
C18	0.054 (3)	0.058 (3)	0.056 (3)	−0.015 (2)	−0.002 (2)	−0.004 (2)
C19	0.128 (6)	0.183 (8)	0.100 (5)	−0.103 (6)	−0.023 (5)	0.004 (6)
C20	0.102 (6)	0.174 (9)	0.152 (8)	0.012 (6)	0.013 (5)	0.040 (7)
O1	0.077 (2)	0.089 (3)	0.069 (2)	−0.028 (2)	0.0101 (18)	−0.037 (2)
O2	0.060 (2)	0.086 (3)	0.100 (3)	−0.036 (2)	−0.0207 (19)	0.017 (2)
O3	0.077 (2)	0.064 (2)	0.077 (2)	−0.0126 (18)	−0.0220 (18)	0.0174 (19)
O4	0.107 (3)	0.074 (3)	0.103 (3)	0.013 (2)	0.057 (2)	0.006 (2)
O5	0.083 (3)	0.078 (3)	0.087 (2)	0.026 (2)	0.030 (2)	−0.004 (2)

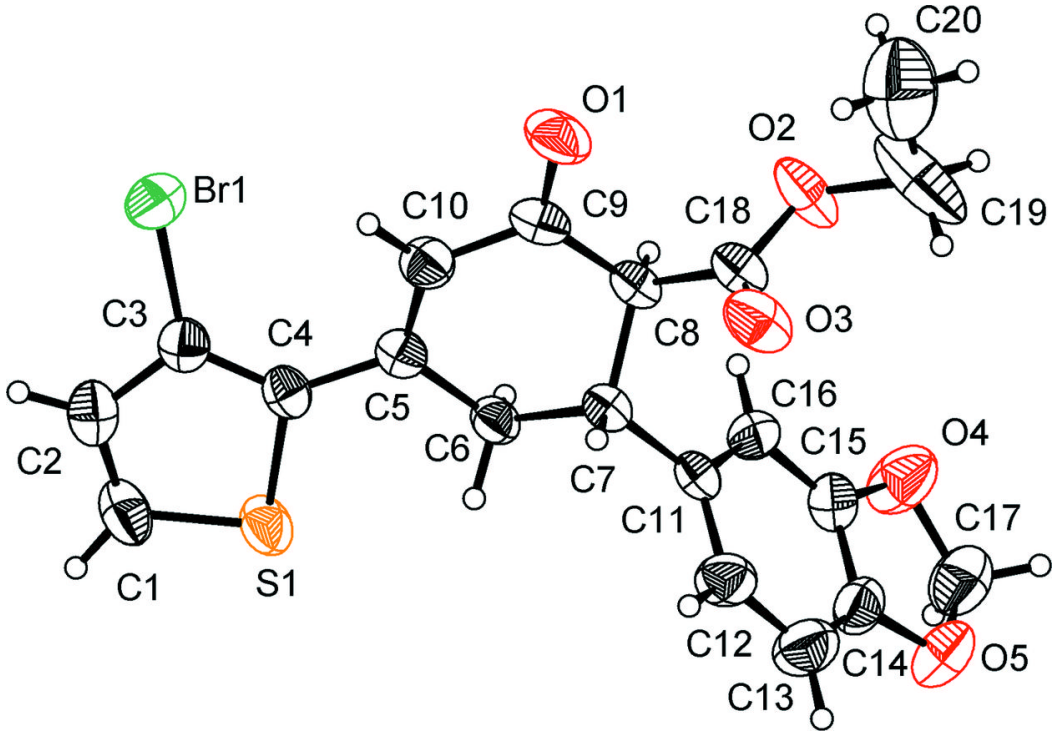
Geometric parameters (Å, °)

Br1—C3	1.883 (4)	C11—C16	1.393 (5)
S1—C1	1.686 (5)	C12—C13	1.385 (7)

S1—C4	1.736 (4)	C12—H12	0.9300
C1—C2	1.335 (7)	C13—C14	1.352 (7)
C1—H1	0.9300	C13—H13	0.9300
C2—C3	1.398 (6)	C14—C15	1.365 (6)
C2—H2	0.9300	C14—O5	1.370 (5)
C3—C4	1.369 (6)	C15—C16	1.359 (6)
C4—C5	1.458 (5)	C15—O4	1.379 (5)
C5—C10	1.339 (5)	C16—H16	0.9300
C5—C6	1.519 (5)	C17—O5	1.413 (7)
C6—C7	1.535 (5)	C17—O4	1.420 (6)
C6—H6A	0.9700	C17—H17A	0.9700
C6—H6B	0.9700	C17—H17B	0.9700
C7—C11	1.512 (5)	C18—O3	1.194 (5)
C7—C8	1.523 (5)	C18—O2	1.321 (5)
C7—H7	0.9800	C19—C20	1.391 (10)
C8—C18	1.508 (6)	C19—O2	1.527 (8)
C8—C9	1.518 (6)	C19—H19A	0.9700
C8—H8	0.9800	C19—H19B	0.9700
C9—O1	1.221 (5)	C20—H20A	0.9600
C9—C10	1.445 (6)	C20—H20B	0.9600
C10—H10	0.9300	C20—H20C	0.9600
C11—C12	1.377 (6)		
C1—S1—C4	92.6 (2)	C12—C11—C7	119.9 (4)
C2—C1—S1	112.4 (4)	C16—C11—C7	121.3 (4)
C2—C1—H1	123.8	C11—C12—C13	122.7 (5)
S1—C1—H1	123.8	C11—C12—H12	118.7
C1—C2—C3	112.4 (4)	C13—C12—H12	118.7
C1—C2—H2	123.8	C14—C13—C12	117.1 (5)
C3—C2—H2	123.8	C14—C13—H13	121.5
C4—C3—C2	114.5 (4)	C12—C13—H13	121.5
C4—C3—Br1	126.7 (3)	C13—C14—C15	121.1 (5)
C2—C3—Br1	118.8 (3)	C13—C14—O5	128.3 (5)
C3—C4—C5	133.3 (4)	C15—C14—O5	110.6 (4)
C3—C4—S1	108.2 (3)	C16—C15—C14	122.6 (4)
C5—C4—S1	118.6 (3)	C16—C15—O4	128.4 (4)
C10—C5—C4	123.3 (4)	C14—C15—O4	108.9 (4)
C10—C5—C6	119.2 (4)	C15—C16—C11	117.7 (4)
C4—C5—C6	117.5 (3)	C15—C16—H16	121.2
C5—C6—C7	112.7 (3)	C11—C16—H16	121.2
C5—C6—H6A	109.0	O5—C17—O4	108.3 (4)
C7—C6—H6A	109.0	O5—C17—H17A	110.0
C5—C6—H6B	109.0	O4—C17—H17A	110.0
C7—C6—H6B	109.0	O5—C17—H17B	110.0
H6A—C6—H6B	107.8	O4—C17—H17B	110.0
C11—C7—C8	113.9 (3)	H17A—C17—H17B	108.4
C11—C7—C6	110.9 (3)	O3—C18—O2	125.7 (4)
C8—C7—C6	109.9 (3)	O3—C18—C8	123.4 (4)
C11—C7—H7	107.3	O2—C18—C8	110.9 (4)
C8—C7—H7	107.3	C20—C19—O2	101.7 (8)

C6—C7—H7	107.3	C20—C19—H19A	111.4
C18—C8—C9	108.8 (3)	O2—C19—H19A	111.4
C18—C8—C7	111.1 (3)	C20—C19—H19B	111.4
C9—C8—C7	110.8 (3)	O2—C19—H19B	111.4
C18—C8—H8	108.7	H19A—C19—H19B	109.3
C9—C8—H8	108.7	C19—C20—H20A	109.5
C7—C8—H8	108.7	C19—C20—H20B	109.5
O1—C9—C10	120.9 (4)	H20A—C20—H20B	109.5
O1—C9—C8	120.5 (4)	C19—C20—H20C	109.5
C10—C9—C8	118.6 (4)	H20A—C20—H20C	109.5
C5—C10—C9	123.9 (4)	H20B—C20—H20C	109.5
C5—C10—H10	118.0	C18—O2—C19	115.9 (5)
C9—C10—H10	118.0	C15—O4—C17	105.5 (4)
C12—C11—C16	118.8 (4)	C14—O5—C17	105.2 (4)

Fig. 1


C20
O1
O2
Br1
C10
C9
C18
C19
C3
C4
C8
O3
C5
C16
C6
C15
O4
C2
C7
C11
C17
C1
S1
C12
C14
O5
C13