



Crystal structure of dibenzo[*c,e*]thiepine-5(7*H*)-thione

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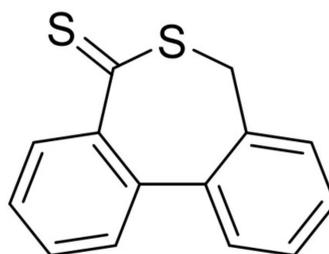
Edited by A. V. Yatsenko, Moscow State University, Russia

Keywords: crystal structure; thiepine; thione; molecular conformation; C—H...S interactions.**CCDC reference:** 2216808**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound, C₁₄H₁₀S₂, was prepared from dibenzo[*c,e*]oxepine-5(7*H*)-one and Lawesson's reagent in refluxing toluene. Pink blocks were grown by slow evaporation from petroleum ether. The resulting crystal structure resides in the orthorhombic space group *Pbca* with *Z* = 8 and *Z'* = 1. The structure is comprised of a network of C—H...S and C—H... π interactions. No π – π interactions between ring moieties were observed, most likely due to the lack of molecular planarity.

1. Chemical context

Ring-opening polymerization is a method of stepwise chain-growth polymerization that can be accessed through a variety of ionic, organometallic, organocatalytic, and radical mechanisms. Of these, radical ring-opening polymerization (rROP) has become popular as it utilizes the benefits of the radical process *via* ease of use and mild reaction conditions (Tardy *et al.*, 2017). Cyclic thioesters, dithionoesters, and dithioesters are commonly used in rROP and have been recently demonstrated in the preparation of a new class of fully degradable polymers (Spick *et al.*, 2020; Purohit *et al.*, 2022; Smith *et al.*, 2019; Kiel *et al.*, 2022; Bingham & Roth, 2019). Specifically, dithioesters are of interest because of their long history of use as reversible addition-fragmentation chain-transfer (RAFT) agents for controlled free-radical polymerization (Perrier, 2017). Herein, we report the crystal structure of a cyclic dithioester, dibenzo[*c,e*]thiepine-5(7*H*)-thione.



2. Structural commentary

The crystal structure of the title compound (Fig. 1) resides in the orthorhombic space group *Pbca* with *Z* = 8, having one molecule per asymmetric unit (*Z'* = 1). Similarly, dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(5*H*)-thione crystallized in the monoclinic space group *P2₁/n* (Peters *et al.*, 2000) and the closely related

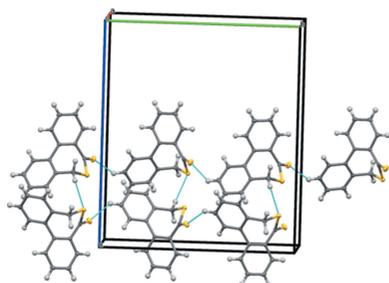
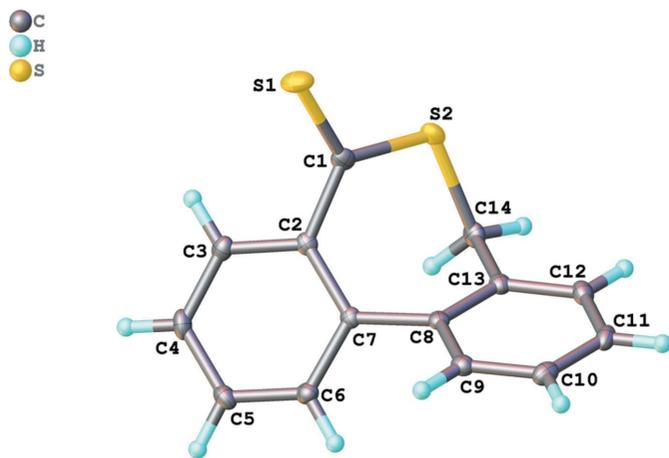


Table 1
 Selected geometric parameters (Å, °).

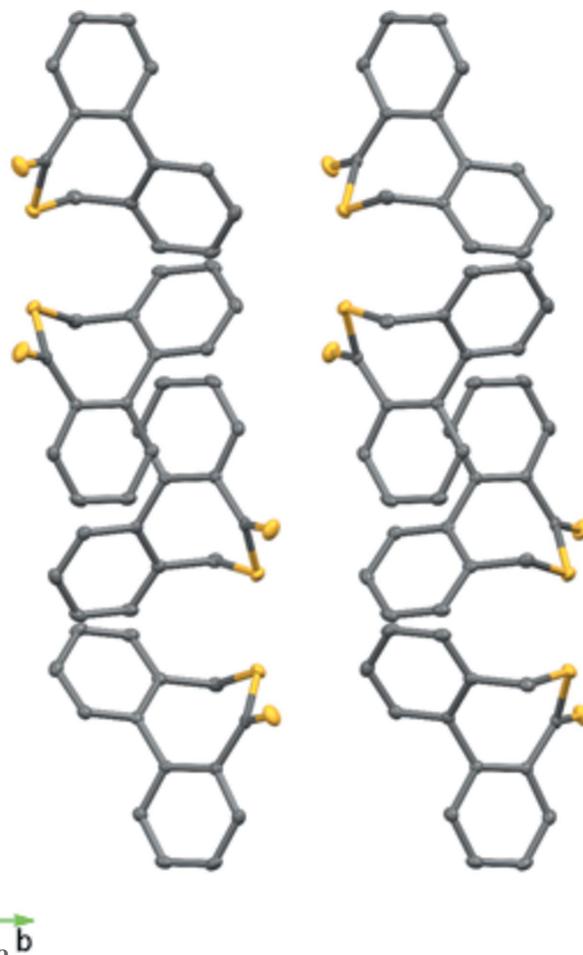
S1—C1	1.645 (12)	C2—C7	1.412 (15)
S2—C1	1.726 (9)	C7—C8	1.483 (9)
S2—C14	1.819 (13)	C8—C13	1.401 (7)
C1—C2	1.482 (8)	C13—C14	1.506 (18)
C1—S2—C14	104.2 (5)	C2—C7—C8	124.4 (3)
S1—C1—S2	116.1 (4)	C13—C8—C7	120.9 (6)
C2—C1—S1	122.4 (2)	C8—C13—C14	119.0 (3)
C2—C1—S2	121.4 (5)	C12—C13—C14	121.1 (4)
C3—C2—C1	116.5 (6)	C13—C14—S2	109.5 (7)
C7—C2—C1	123.9 (4)		

dibenzo[*c,e*]oxepine-5(*7H*)-thione (Smith *et al.*, 2019; Yang *et al.*, 2019) crystallized in the *Pbca* space group. The bond lengths in the title molecule are typical of this type of compound, whereas the angles within the seven-membered ring indicate that this ring is slightly strained (see Table 1). Interestingly, the torsion angle S1—C1—C2—C3 for the title compound is 46.4 (3)°, which lies in between those in dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(*5H*)-thione [52.6 (3)°] and dibenzo[*c,e*]oxepine-5(*7H*)-thione [42.38 (12)°]. Additionally, the angle involving the thio S2 atom, C1—S2—C14, for the title compound is 104.2 (5)° (Table 1), which is comparable to the same angle in dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(*5H*)-thione [103.64 (12)°]. However, dibenzo[*c,e*]oxepine-5(*7H*)-thione exhibits a larger angle of 118.73 (8)° with the replacement of the sulfur atom by an oxygen. The dibenzo ring system in the title compound exhibits a dihedral angle of 50.8 (5)°, which is significantly smaller than in dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(*5H*)-thione. The comparable aromatic rings in the naphthalene-containing structure are observed to have a dihedral angle of 65.17 (8)°, whereas the whole naphthalene systems make an angle of 68.10 (4)°. In comparison, in dibenzo[*c,e*]oxepine-5(*7H*)-thione, the dihedral angle between the respective ring systems is 41.02 (3)°, which is the smallest dihedral angle out of the three compounds highlighted.


Figure 1
 The molecular structure of dibenzo[*c,e*]thiepine-5(*7H*)-thione. Displacement ellipsoids are shown at the 50% probability level.

3. Supramolecular features

A view of the crystal packing of the title compound is presented in Fig. 2. The molecules pack in an alternating pattern that does not exhibit any π - π interactions between ring planes of neighboring molecules. This phenomenon is most probably due to lack of molecular planarity. For example, the dihedral angle between the two dibenzo rings is 122.7 (5)°. In comparison, both dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(*5H*)-thione [3.908 (2) Å; Peters *et al.*, 2000] and dibenzo[*c,e*]oxepine-5(*7H*)-thione [3.7742 (9) Å] exhibit weak π - π interactions between neighboring rings. Therefore, the title compound can be considered an outlier as it packs in a way to minimize any such interactions. Rather, the title compound packs in a way to maximize C—H...S interactions (Fig. 3) between adjacent molecules. The shortest C—H...S contacts are 2.94 Å [C14—H14B...S2($\frac{1}{2} + x, y, \frac{3}{2} - z$)] and 2.97 Å [C10—H10...S1($\frac{1}{2} - x, -\frac{1}{2} + y, z$)]. Comparing dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(*5H*)-thione, there is a slightly shorter contact of 2.86 Å of the thioketone sulfur to a neighboring hydrogen atom. By comparison, the lack of contacts is not abnormal as the only notable short C—H...O contact for the oxepine compound is 2.57 Å, which is significantly shorter in comparison to its sulfur counterparts. Lastly, the title compound


Figure 2
 The packing view of dibenzo[*c,e*]thiepine-5(*7H*)-thione along the *a*-axis direction. Hydrogen atoms omitted for clarity.

exhibits close C—H·· π interactions: C12—H12··Cg2($\frac{1}{2} + x$, $y, \frac{3}{2} - z$) of 2.94 Å and C4—H4··Cg2($-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$) of 2.93 Å, where Cg2 is the centroid of the C8—C13 aromatic ring, which is longer than a similar contact in dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(5*H*)-thione (2.67 Å). In conclusion, both dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(5*H*)-thione and dibenzo[*c,e*]-5(7*H*)-thione utilize π - π interactions in addition to their respective short contacts in packing, whereas the title compound solely relies on its weaker C—H··S and C—H·· π interactions.

4. Database survey

A search of the Cambridge Structural Database (CSD, version of March 2022; Groom *et al.*, 2016) for dibenzothiepines yielded one result. The bond lengths and angles in the title molecule are consistent with the previously reported crystal structure of dinaphth[2,1-*e*:1',2'-*e*]thiepin-3-(5*H*)-thione (FUQHAA; Peters *et al.*, 2000). This compound was compared to the title compound in the previous sections.

5. Synthesis and crystallization

The synthesis of dibenzo[*c,e*]oxepine-5(7*H*)-one was adapted from the procedure reported by Bingham & Roth (2019). Lawesson's reagent (7.65 g, 18.9 mmol, 2.2 eq) was added to a solution of dibenzo[*c,e*]oxepine-5(7*H*)-one (1.81 g, 8.6 mmol) in anhydrous toluene and the reaction was refluxed for 72 h. The solution was filtered and the filtrate was concentrated *in vacuo*. The resulting orange solid was purified using column chromatography (hexane—EtOAc, 4:1) to afford a red oil that solidified upon standing. The red solid was further purified by recrystallization from petroleum ether to afford a red crystalline solid (0.465 g, 22%). Pink crystals of the title compound suitable for single-crystal X-ray diffraction were obtained after slow evaporation of petroleum ether.

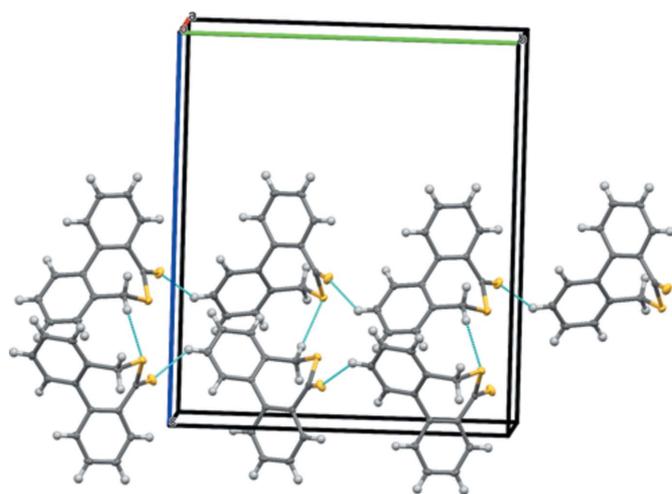


Figure 3
View of intermolecular C—H··S interactions in the title structure.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₀ S ₂
<i>M_r</i>	242.34
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.84 (7), 16.0 (2), 18.51 (12)
<i>V</i> (Å ³)	2315 (39)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.43
Crystal size (mm)	0.17 × 0.14 × 0.09
Data collection	
Diffractometer	Bruker D8
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.384, 0.431
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	30500, 2664, 2154
<i>R_{int}</i>	0.059
(sin θ/λ) _{max} (Å ⁻¹)	0.651
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.088, 1.04
No. of reflections	2664
No. of parameters	145
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.42, -0.28

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. All H atoms were placed in calculated positions (0.95–0.99 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

7. Distribution Statement A

Distribution Statement A. Approved for public release. Distribution is unlimited.

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supporting information

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Crystal structure of dibenzo[*c,e*]thiepine-5(7*H*)-thione

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Computing details

Data collection: *APEX3* (Bruker, 2017); cell refinement: *SAINTE* (Bruker, 2017); data reduction: *SAINTE* (Bruker, 2017); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Dibenzo[*c,e*]thiepine-5(7*H*)-thione

Crystal data

$C_{14}H_{10}S_2$	$D_x = 1.390 \text{ Mg m}^{-3}$
$M_r = 242.34$	Mo $K\alpha$ radiation, $\lambda = 0.71076 \text{ \AA}$
Orthorhombic, <i>Pbca</i>	Cell parameters from 6808 reflections
$a = 7.84 (7) \text{ \AA}$	$\theta = 2.8\text{--}27.5^\circ$
$b = 16.0 (2) \text{ \AA}$	$\mu = 0.43 \text{ mm}^{-1}$
$c = 18.51 (12) \text{ \AA}$	$T = 100 \text{ K}$
$V = 2315 (39) \text{ \AA}^3$	Block, pink
$Z = 8$	$0.17 \times 0.14 \times 0.09 \text{ mm}$
$F(000) = 1008$	

Data collection

Bruker D8 diffractometer	30500 measured reflections
Radiation source: microsource	2664 independent reflections
Detector resolution: 7.39 pixels mm^{-1}	2154 reflections with $I > 2\sigma(I)$
ω and ϕ scans	$R_{\text{int}} = 0.059$
Absorption correction: multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.384$, $T_{\text{max}} = 0.431$	$h = -10 \rightarrow 10$
	$k = -20 \rightarrow 20$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 1.959P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2664 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
145 parameters	$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
Primary atom site location: dual	

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.22706 (6)	0.45127 (3)	0.62216 (3)	0.02342 (14)
S2	0.55925 (6)	0.43034 (3)	0.68343 (2)	0.01708 (12)
C1	0.4180 (2)	0.40955 (11)	0.61419 (10)	0.0146 (4)
C2	0.4711 (2)	0.36200 (11)	0.54916 (9)	0.0126 (3)
C3	0.4331 (2)	0.39856 (11)	0.48215 (10)	0.0151 (4)
H3	0.378333	0.451651	0.480640	0.018*
C4	0.4742 (2)	0.35855 (12)	0.41837 (10)	0.0171 (4)
H4	0.453373	0.385195	0.373326	0.021*
C5	0.5463 (2)	0.27895 (12)	0.42054 (10)	0.0170 (4)
H5	0.573181	0.250763	0.376789	0.020*
C6	0.5790 (2)	0.24074 (12)	0.48594 (9)	0.0146 (4)
H6	0.624863	0.185631	0.486547	0.017*
C7	0.5458 (2)	0.28150 (11)	0.55145 (9)	0.0119 (3)
C8	0.5867 (2)	0.23546 (11)	0.61885 (9)	0.0124 (3)
C9	0.5363 (2)	0.15165 (11)	0.62688 (9)	0.0147 (4)
H9	0.468183	0.125926	0.590690	0.018*
C10	0.5849 (2)	0.10611 (12)	0.68701 (10)	0.0171 (4)
H10	0.549682	0.049405	0.691907	0.020*
C11	0.6843 (2)	0.14257 (12)	0.73997 (10)	0.0172 (4)
H11	0.717350	0.111077	0.781216	0.021*
C12	0.7357 (2)	0.22559 (12)	0.73271 (9)	0.0168 (4)
H12	0.804544	0.250574	0.769049	0.020*
C13	0.6873 (2)	0.27230 (12)	0.67274 (9)	0.0136 (4)
C14	0.7404 (2)	0.36256 (12)	0.66461 (9)	0.0165 (4)
H14A	0.781845	0.372603	0.614831	0.020*
H14B	0.834472	0.375278	0.698553	0.020*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0177 (2)	0.0222 (3)	0.0303 (3)	0.0043 (2)	0.0017 (2)	-0.0084 (2)
S2	0.0214 (2)	0.0154 (2)	0.0144 (2)	-0.00114 (18)	-0.00091 (18)	-0.00374 (17)
C1	0.0175 (9)	0.0102 (8)	0.0162 (8)	-0.0024 (7)	0.0009 (7)	-0.0005 (7)
C2	0.0107 (8)	0.0137 (8)	0.0135 (8)	-0.0037 (7)	-0.0005 (7)	-0.0001 (7)
C3	0.0136 (8)	0.0140 (8)	0.0176 (8)	-0.0013 (7)	-0.0034 (7)	0.0015 (7)
C4	0.0162 (9)	0.0218 (10)	0.0134 (8)	-0.0041 (8)	-0.0035 (7)	0.0053 (7)
C5	0.0158 (9)	0.0233 (10)	0.0120 (8)	-0.0013 (8)	0.0006 (7)	-0.0022 (7)
C6	0.0127 (8)	0.0155 (9)	0.0155 (8)	0.0015 (7)	-0.0007 (7)	-0.0011 (7)
C7	0.0091 (8)	0.0145 (8)	0.0120 (8)	-0.0018 (7)	-0.0010 (6)	-0.0001 (6)

C8	0.0102 (8)	0.0149 (9)	0.0123 (8)	0.0017 (7)	0.0020 (6)	-0.0008 (7)
C9	0.0124 (8)	0.0167 (9)	0.0151 (8)	0.0002 (7)	0.0006 (7)	-0.0017 (7)
C10	0.0152 (9)	0.0159 (9)	0.0200 (9)	0.0009 (7)	0.0041 (7)	0.0029 (7)
C11	0.0141 (9)	0.0233 (10)	0.0143 (8)	0.0052 (7)	0.0017 (7)	0.0051 (7)
C12	0.0137 (8)	0.0242 (10)	0.0124 (8)	0.0009 (8)	0.0003 (7)	0.0000 (7)
C13	0.0114 (8)	0.0169 (9)	0.0126 (8)	0.0011 (7)	0.0014 (6)	-0.0007 (7)
C14	0.0136 (8)	0.0206 (10)	0.0153 (8)	-0.0028 (7)	-0.0035 (7)	-0.0014 (7)

Geometric parameters (Å, °)

S1—C1	1.645 (12)	C7—C8	1.483 (9)
S2—C1	1.726 (9)	C8—C13	1.401 (7)
S2—C14	1.819 (13)	C8—C9	1.402 (16)
C1—C2	1.482 (8)	C9—C10	1.383 (8)
C2—C3	1.403 (8)	C9—H9	0.9500
C2—C7	1.412 (15)	C10—C11	1.381 (7)
C3—C4	1.380 (8)	C10—H10	0.9500
C3—H3	0.9500	C11—C12	1.391 (16)
C4—C5	1.391 (15)	C11—H11	0.9500
C4—H4	0.9500	C12—C13	1.390 (8)
C5—C6	1.379 (8)	C12—H12	0.9500
C5—H5	0.9500	C13—C14	1.506 (18)
C6—C7	1.400 (8)	C14—H14A	0.9900
C6—H6	0.9500	C14—H14B	0.9900
C1—S2—C14	104.2 (5)	C13—C8—C7	120.9 (6)
S1—C1—S2	116.1 (4)	C9—C8—C7	120.1 (4)
C2—C1—S1	122.4 (2)	C10—C9—C8	120.6 (4)
C2—C1—S2	121.4 (5)	C10—C9—H9	119.7
C3—C2—C7	119.5 (3)	C8—C9—H9	119.7
C3—C2—C1	116.5 (6)	C11—C10—C9	120.4 (6)
C7—C2—C1	123.9 (4)	C11—C10—H10	119.8
C4—C3—C2	121.0 (6)	C9—C10—H10	119.8
C4—C3—H3	119.5	C10—C11—C12	119.7 (3)
C2—C3—H3	119.5	C10—C11—H11	120.1
C3—C4—C5	119.5 (4)	C12—C11—H11	120.1
C3—C4—H4	120.2	C13—C12—C11	120.6 (4)
C5—C4—H4	120.2	C13—C12—H12	119.7
C6—C5—C4	120.3 (3)	C11—C12—H12	119.7
C6—C5—H5	119.9	C12—C13—C8	119.8 (6)
C4—C5—H5	119.9	C8—C13—C14	119.0 (3)
C5—C6—C7	121.4 (6)	C12—C13—C14	121.1 (4)
C5—C6—H6	119.3	C13—C14—S2	109.5 (7)
C7—C6—H6	119.3	C13—C14—H14A	109.8
C6—C7—C2	118.2 (4)	S2—C14—H14A	109.8
C6—C7—C8	117.3 (7)	C13—C14—H14B	109.8
C2—C7—C8	124.4 (3)	S2—C14—H14B	109.8
C13—C8—C9	118.9 (3)	H14A—C14—H14B	108.2