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Dibenzo[*b,e*]thiepin-11(6*H*)-one

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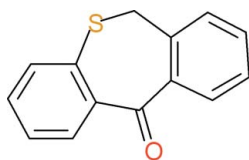
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Key indicators: single-crystal X-ray study; $T = 110$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.039; wR factor = 0.104; data-to-parameter ratio = 9.1.

In the title compound, $\text{C}_{14}\text{H}_{10}\text{OS}$, the seven-membered thiepin ring adopts a distorted boat conformation with the dihedral angle between the mean planes of the two fused benzene rings being $56.5(1)^\circ$.

Related literature

For the biological and chiroptical properties of dibenzo[*c,e*]thiepine derivatives, see: Rajsner *et al.* (1969, 1971); Truce & Emrick (1956); Tomascovic *et al.* (2000). For spectral, structural and theoretical studies of eight related 6-arylidene-dibenzo[*b,e*]thiepin-11-one-5,5-dioxides, see: Kolehmainen *et al.* (2007). For DFT calculations and the *GAUSSIAN03* program package, see: Schmidt & Polik (2007); Frisch *et al.* (2004). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{10}\text{OS}$
 $M_r = 226.28$

Orthorhombic, *Pna*2₁
 $a = 14.6208(11)$ Å

$b = 4.3503(3)$ Å
 $c = 16.9023(13)$ Å
 $V = 1075.07(14)$ Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.27$ mm⁻¹
 $T = 110$ K
 $0.47 \times 0.42 \times 0.12$ mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{\min} = 0.769$, $T_{\max} = 1.000$

2124 measured reflections
1322 independent reflections
1291 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.104$
 $S = 1.06$
1322 reflections
145 parameters
1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³
Absolute structure: Flack (1983),
242 Friedel pairs
Flack parameter: $-0.57(13)$

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *WebMOPro* (Schmidt & Polik, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2983).

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supplementary materials

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Dibenzo[*b,e*]thiepin-11(6*H*)-one

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Comment

The title compound is used as an intermediate for the synthesis of dosulepin, which is an antidepressant of the tricyclic family. Dosulepin works by preventing serotonin and noradrenaline from being reabsorbed in the brain. This helps prolong the mood lightening effect of any released noradrenaline and serotonin, thus relieving depression. The dibenzo[*c,e*]thiepine derivatives (Truce *et al.*, 1956) exhibit remarkable chiroptical properties (Tomascovic *et al.*, 2000). The dibenzo[*b,e*]thiepin-5,5-dioxide derivatives are known to possess antihistaminic and antiallergenic activities (Rajsner *et al.*, 1971). In addition, by aminoalkylation of 6,11-dihydrodibenzo[*b,e*]thiepin-5,5-dioxide and the corresponding 11-ketone, compounds with neurotropic and psychotropic activities have been reported (Rajsner *et al.*, 1969). In addition, the comparative NMR and IR spectral, X-ray structural and theoretical studies of eight 6-arylidenedibenzo[*b,e*]thiepin-11-one-5,5-dioxides have been reported (Kolehmainen *et al.*, 2007). In view of the importance of thiepinines, this paper reports the crystal structure of the title compound.

The seven-membered thiepin ring adopts a distorted boat conformation with the dihedral angle between the mean planes of the two fused benzene rings measuring 56.5 (1)° (Fig. 1). This conformation is assisted by sp^3 hybridization of atom C8 within the ring. The ketone oxygen atom (O) lies in an equatorial position from the ring on opposite sides of the C8 and S atoms [C3—C2—C1—O = 31.1 (4)° and C13—C14—C1—O = -50.7 (4)°]. Bond lengths and bond angles are all within expected ranges (Allen, 2002).

Following a geometry optimization density functional theory calculation (Schmidt & Polik, 2007), *in vacuo*, at the B3LYP 6-31-G(*d*) level with the GAUSSIAN03 program package (Frisch *et al.*, 2004) the angle between the mean planes of the two benzene rings becomes 46.2 (6)°, a decrease of 14.2 (5)°. The C3—C2—C1—O and C13—C14—C1—O torsion angles become 12.8 (2)° and -36.9 (1)°, a decrease of 18.3 (2)° and 13.8 (3)°, respectively.

Experimental

The title compound was obtained as a gift sample from *R. L. Fine Chem*, Bangalore, India. The compound was used without further purification. X-ray quality crystals (m.p. 347–349 K) were obtained by slow evaporation of a solution in methanol.

Refinement

H atoms were placed in their calculated positions and then refined using the riding model with C—H = 0.95–0.99 Å, and with $U_{\text{iso}}(\text{H}) = 1.18\text{--}1.21U_{\text{eq}}(\text{C})$. The absolute structure could not be determined reliably due to the low Friedel pair coverage.

Figures

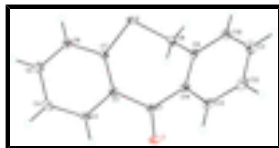


Fig. 1. Molecular structure of the title compound, showing atom-labeling scheme and 50% probability displacement ellipsoids.

Dibenzo[*b,e*]thiepin-11(6*H*)-one

Crystal data

$C_{14}H_{10}OS$

$M_r = 226.28$

Orthorhombic, $Pna2_1$

Hall symbol: $P\ 2c\ -2n$

$a = 14.6208\ (11)\ \text{\AA}$

$b = 4.3503\ (3)\ \text{\AA}$

$c = 16.9023\ (13)\ \text{\AA}$

$V = 1075.07\ (14)\ \text{\AA}^3$

$Z = 4$

$F(000) = 472$

$D_x = 1.398\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1716 reflections

$\theta = 4.0\text{--}73.6^\circ$

$\mu = 0.27\ \text{mm}^{-1}$

$T = 110\ \text{K}$

Plate, colorless

$0.47 \times 0.42 \times 0.12\ \text{mm}$

Data collection

Oxford Diffraction Gemini R CCD diffractometer

Radiation source: fine-focus sealed tube graphite

Detector resolution: $10.5081\ \text{pixels mm}^{-1}$

φ and ω scans

Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)

$T_{\min} = 0.769$, $T_{\max} = 1.000$

2124 measured reflections

1322 independent reflections

1291 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\max} = 26.2^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -11 \rightarrow 17$

$k = -4 \rightarrow 5$

$l = -8 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.104$

$S = 1.06$

1322 reflections

145 parameters

1 restraint

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2 + 0.7978P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.42\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.35\ \text{e \AA}^{-3}$

Absolute structure: Flack (1983), 242 Friedel pairs

Primary atom site location: structure-invariant direct methods Flack parameter: $-0.57(13)$

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.52142 (4)	-0.06772 (16)	0.24929 (6)	0.0178 (2)
O	0.78147 (17)	-0.0883 (7)	0.09651 (19)	0.0321 (7)
C1	0.7100 (2)	0.0006 (8)	0.1263 (2)	0.0200 (7)
C2	0.7074 (2)	0.0905 (7)	0.2121 (2)	0.0180 (7)
C3	0.7902 (2)	0.2143 (7)	0.2405 (2)	0.0227 (7)
H3A	0.8423	0.2129	0.2070	0.027*
C4	0.7980 (2)	0.3374 (9)	0.3154 (2)	0.0256 (8)
H4A	0.8543	0.4237	0.3326	0.031*
C5	0.7227 (2)	0.3339 (9)	0.3654 (2)	0.0244 (7)
H5A	0.7276	0.4167	0.4173	0.029*
C6	0.6408 (2)	0.2104 (7)	0.3401 (2)	0.0192 (7)
H6A	0.5897	0.2100	0.3748	0.023*
C7	0.6316 (2)	0.0853 (6)	0.26388 (19)	0.0161 (7)
C8	0.5289 (2)	-0.2607 (8)	0.1555 (2)	0.0207 (7)
H8A	0.5805	-0.4078	0.1569	0.025*
H8B	0.4720	-0.3796	0.1466	0.025*
C9	0.5423 (2)	-0.0449 (7)	0.0884 (2)	0.0170 (7)
C10	0.4704 (2)	0.0389 (8)	0.0388 (2)	0.0209 (7)
H10A	0.4110	-0.0416	0.0480	0.025*
C11	0.4848 (3)	0.2376 (9)	-0.0235 (2)	0.0266 (8)
H11A	0.4350	0.2961	-0.0563	0.032*
C12	0.5718 (3)	0.3529 (8)	-0.0386 (2)	0.0261 (8)
H12A	0.5814	0.4879	-0.0820	0.031*
C13	0.6447 (2)	0.2706 (8)	0.0099 (2)	0.0222 (7)
H13A	0.7043	0.3476	-0.0006	0.027*
C14	0.6299 (2)	0.0741 (7)	0.0741 (2)	0.0187 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0114 (3)	0.0242 (4)	0.0177 (4)	-0.0023 (3)	0.0028 (3)	-0.0015 (4)

supplementary materials

O	0.0181 (12)	0.0470 (16)	0.0312 (15)	0.0089 (11)	0.0049 (11)	-0.0110 (13)
C1	0.0157 (14)	0.0217 (14)	0.0226 (19)	0.0006 (13)	0.0051 (14)	-0.0056 (14)
C2	0.0163 (15)	0.0174 (14)	0.0203 (17)	0.0046 (11)	0.0009 (13)	0.0016 (13)
C3	0.0113 (12)	0.0297 (15)	0.027 (2)	0.0020 (12)	0.0013 (15)	0.0002 (17)
C4	0.0167 (15)	0.0290 (18)	0.031 (2)	-0.0024 (14)	-0.0047 (15)	-0.0004 (16)
C5	0.0257 (17)	0.0275 (16)	0.0201 (17)	-0.0011 (15)	-0.0046 (15)	-0.0026 (15)
C6	0.0176 (14)	0.0205 (15)	0.0196 (15)	-0.0019 (13)	0.0039 (13)	0.0006 (14)
C7	0.0142 (13)	0.0141 (13)	0.020 (2)	0.0016 (11)	-0.0002 (12)	0.0000 (11)
C8	0.0200 (14)	0.0193 (16)	0.0228 (19)	-0.0038 (12)	-0.0014 (13)	-0.0017 (14)
C9	0.0205 (14)	0.0153 (15)	0.0153 (17)	-0.0009 (12)	-0.0005 (13)	-0.0048 (12)
C10	0.0189 (15)	0.0202 (16)	0.0235 (19)	-0.0007 (13)	-0.0016 (13)	-0.0050 (14)
C11	0.0299 (18)	0.0252 (17)	0.0247 (19)	0.0018 (14)	-0.0070 (15)	-0.0023 (16)
C12	0.0348 (18)	0.0255 (17)	0.0179 (16)	-0.0010 (16)	0.0040 (15)	0.0020 (14)
C13	0.0258 (16)	0.0216 (16)	0.0191 (16)	-0.0033 (13)	0.0075 (14)	-0.0040 (14)
C14	0.0179 (15)	0.0170 (14)	0.0211 (17)	0.0020 (12)	0.0048 (14)	-0.0043 (13)

Geometric parameters (Å, °)

S—C7	1.760 (3)	C6—H6A	0.95
S—C8	1.798 (4)	C8—C9	1.485 (5)
O—C1	1.223 (4)	C8—H8A	0.99
C1—C14	1.500 (5)	C8—H8B	0.99
C1—C2	1.503 (5)	C9—C10	1.394 (5)
C2—C3	1.409 (4)	C9—C14	1.402 (5)
C2—C7	1.413 (4)	C10—C11	1.378 (6)
C3—C4	1.379 (5)	C10—H10A	0.95
C3—H3A	0.95	C11—C12	1.391 (5)
C4—C5	1.388 (5)	C11—H11A	0.95
C4—H4A	0.95	C12—C13	1.392 (5)
C5—C6	1.381 (5)	C12—H12A	0.95
C5—H5A	0.95	C13—C14	1.398 (5)
C6—C7	1.404 (4)	C13—H13A	0.95
C7—S—C8	104.17 (15)	C9—C8—H8A	109.1
O—C1—C14	119.5 (3)	S—C8—H8A	109.1
O—C1—C2	120.1 (3)	C9—C8—H8B	109.1
C14—C1—C2	119.5 (3)	S—C8—H8B	109.1
C3—C2—C7	118.0 (3)	H8A—C8—H8B	107.8
C3—C2—C1	114.0 (3)	C10—C9—C14	119.2 (3)
C7—C2—C1	127.8 (3)	C10—C9—C8	121.6 (3)
C4—C3—C2	122.2 (3)	C14—C9—C8	119.1 (3)
C4—C3—H3A	118.9	C11—C10—C9	120.5 (3)
C2—C3—H3A	118.9	C11—C10—H10A	119.7
C3—C4—C5	119.3 (3)	C9—C10—H10A	119.7
C3—C4—H4A	120.4	C10—C11—C12	120.4 (4)
C5—C4—H4A	120.4	C10—C11—H11A	119.8
C6—C5—C4	120.2 (3)	C12—C11—H11A	119.8
C6—C5—H5A	119.9	C11—C12—C13	120.0 (3)
C4—C5—H5A	119.9	C11—C12—H12A	120.0
C5—C6—C7	121.3 (3)	C13—C12—H12A	120.0

C5—C6—H6A	119.4	C12—C13—C14	119.7 (3)
C7—C6—H6A	119.4	C12—C13—H13A	120.1
C6—C7—C2	119.1 (3)	C14—C13—H13A	120.1
C6—C7—S	111.3 (2)	C13—C14—C9	120.1 (3)
C2—C7—S	129.6 (3)	C13—C14—C1	117.8 (3)
C9—C8—S	112.7 (2)	C9—C14—C1	122.2 (3)
O—C1—C2—C3	31.1 (4)	S—C8—C9—C10	-101.8 (3)
C14—C1—C2—C3	-137.8 (3)	S—C8—C9—C14	79.1 (3)
O—C1—C2—C7	-153.8 (3)	C14—C9—C10—C11	-0.3 (5)
C14—C1—C2—C7	37.3 (5)	C8—C9—C10—C11	-179.4 (3)
C7—C2—C3—C4	-2.1 (5)	C9—C10—C11—C12	1.2 (5)
C1—C2—C3—C4	173.4 (3)	C10—C11—C12—C13	-0.7 (6)
C2—C3—C4—C5	1.5 (5)	C11—C12—C13—C14	-0.6 (5)
C3—C4—C5—C6	-0.5 (5)	C12—C13—C14—C9	1.4 (5)
C4—C5—C6—C7	0.2 (5)	C12—C13—C14—C1	-177.9 (3)
C5—C6—C7—C2	-0.9 (5)	C10—C9—C14—C13	-1.0 (5)
C5—C6—C7—S	177.7 (3)	C8—C9—C14—C13	178.1 (3)
C3—C2—C7—C6	1.8 (4)	C10—C9—C14—C1	178.4 (3)
C1—C2—C7—C6	-173.1 (3)	C8—C9—C14—C1	-2.5 (5)
C3—C2—C7—S	-176.6 (2)	O—C1—C14—C13	-50.7 (4)
C1—C2—C7—S	8.5 (5)	C2—C1—C14—C13	118.2 (4)
C8—S—C7—C6	-172.2 (2)	O—C1—C14—C9	129.9 (4)
C8—S—C7—C2	6.3 (3)	C2—C1—C14—C9	-61.1 (4)
C7—S—C8—C9	-67.1 (3)		

Fig. 1

