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1,2-Dibromo-5-(4-tolylsulfonyl)-2,2a,4a,5,7a,7b-hexahydro-1*H*-7-oxa-5-azacyclobuta[e]inden-6-one

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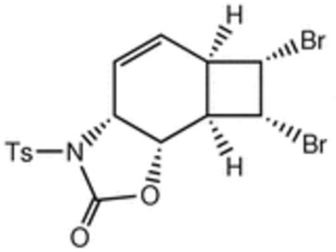
Key indicators: single-crystal X-ray study; *T* = 293 K; mean σ(C–C) = 0.008 Å; *R* factor = 0.099; *wR* factor = 0.144; data-to-parameter ratio = 24.4.

The title compound $C_{16}H_{15}Br_2NO_4S$, contains a central cyclohexene ring with cyclobutane and oxazolidinone groups fused to it. All the substituents, including the oxazolidinone group and the bromine atoms, are on the same side of the fused four- and six-membered rings (*syn* conformation). The two bromine atoms are *cis* to each other.

Related literature

For related literature, see: Vasilyev *et al.* (2001); Balci (1981); Boshe & Huisgen (1965); Gözel *et al.* (1991); Huisgen & Gasteiger (1972); Kara *et al.* (1994); Kara & Balci (2003); Kelebekli *et al.* (2005); Kelebekli *et al.* (2006); Lysek & Vogel (2006); Paul *et al.* (2002); Reppe *et al.* (1948); Seçen *et al.* (1990); Şahin *et al.* (2006); Trost *et al.* (1992); Trost & Van Vranken (1993).



Experimental

Crystal data

$C_{16}H_{15}Br_2NO_4S$
M_r = 477.17
Monoclinic, $P2_1/n$
a = 10.8513 (4) Å
b = 6.0019 (3) Å
c = 26.7246 (7) Å
β = 90.232 (2)°
V = 1740.52 (12) Å^3
Z = 4
Mo *Kα* radiation
μ = 4.80 mm^{-1}
T = 293 (2) K
0.32 × 0.21 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID S diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.310, $T_{\max}$ = 0.383
44718 measured reflections
5328 independent reflections
4398 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.097

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.099
$wR(F^2)$ = 0.144
S = 1.39
5328 reflections
218 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\min}$ = −0.49 e Å^{-3}

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AV3083).

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supplementary materials

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1,2-Dibromo-5-(4-tolylsulfonyl)-2,2a,4a,5,7a,7b-hexahydro-1*H*-7-oxa-5-azacyclobuta[*e*]inden-6-one

E. Sahin, **L. Kelebekli**, **Y. Kara**, **M. Çelik** and **M. Balci**

Comment

Recently, we successfully used cyclooctatetraene as starting material for synthesis of various stereospecific cyclitol isomers and their aminocyclitol derivatives (Kara *et al.*, 1994; Kelebekli *et al.*, 2005, 2006). In addition, some aminocyclitols have shown interesting inhibitor activities towards glycosidases (Paul *et al.*, 2002; Lysek & Vogel 2006). It is known that both cis- and trans-7,8-dichloro-cycloocta-1,3,5-triene are obtained by chlorination of cyclooctatetraene 1 (Reppe *et al.*, 1948; Gözel *et al.*, 1991;Şahin *et al.*, 2006) (Scheme). For synthesis of the aminoconduritol derivative, we performed bromination of cyclooctatetraene 1 in ice bath (Boshe & Huisgen, 1965; Huisgen & Gasteiger, 1972). The bromination product 2 was heated in CCl_4 at 323 K to form 3. The photooxygenation of 3 and its reduction of O—O bond with thiourea resulted in formation of 5 (Balci, 1981; Seçen *et al.*, 1990; Kara & Balci, 2003; Kelebekli *et al.*, 2005, 2006). Pd(0)-catalyzed reactions provide the selective entry to amino alcohols with various regio- and stereoselectivity. Recently, vinyl oxazolidone-2-one has been synthesized by stereoselective Pd(0)-catalyzed reaction with cis-2-alkene-1,4-diol in a single step (Trost *et al.*, 1992; Trost & Van Vranken, 1993). Using this method, oxazolidinone 6 b was synthesized from 5 b. The exact configuration of compound 6 b was determined by ^{1}H and ^{13}C- NMR spectra and an X-ray diffraction analysis. The resolved structure provides information on the stereochemical course of the cis-brom atoms, namely, both bromine atoms are cis to each other. It is known that bromination is a stereoscpecific anti-addition. In the light of all this findings, one can conclude that formation of cis-bromide occurrs during bromination of cyclooctatetraene 1 as a minor product along with major trans adduct. In order to confirm this unexpected result again, the bromination of cyclooctatetraene 1 was repeated, and consecutive yield of cis-bromide was 5-10%.

The molecular structure of 6 b is shown in Fig. 1, and the bond lengths and angles are listed in Table 1. A s reported earlier, after the bromination of cyclooctatetraene 1, cis-bromide product was observed (Boshe & Huisgen, 1965; Huisgen & Gasteiger, 1972), but this type of adducts was not investigated in detail.

Compound 6 b contains a central cyclohexene ring with a cyclobutane and oxazolidinone moieties fused to it. The Br atoms have cis stereochemistry, in which Br1—C15 [1.926 (5)] and Br2—C16 [(1.933 (3)]Å bond lengths are comparable with the Br—C (1.94 (1), 1.93 (1) Å) bond lengths in the dibromotetraacetate compound (Kara *et al.*, 1994), but there the Br atoms have trans

configuration. Because of cis configuration of the Br atoms in compound 5 b, oxazolidinone moiety leads to formation of the only product 6 b. All the substituents, including the oxazolidinone moiety and the bromine atoms are on the same side of the bicycle (syn conformation). In addition to this, the cyclobutane and the oxazolidinone rings have trans stereochemistry. The cyclobutane moiety is appreciably folded with C—C distances in the range 1.542 (7)-1.551 (7) Å. Due to the strong electronegativity of the Cl atoms, this range is larger [1.534 (3)-1.567 (3) Å] in the (1SR,2SR,3SR,4RS,5RS,6RS,7SR,8RS)-7,8-Dichlorobicyclo[4.2.0] octa-2,3,4,5-tetrayl tetraacetate structure Şahin *et al.*, 2006). Finally the cyclohexene ring adopts a half-chair conformation with puckering parameters Q_T=0.283 (5) Å, θ =52.0 (2)and φ=84.3 (4) °. Electron localization was also found at the C13—C14 bond with a length of 1.310 (7)Å which is appreciably shorter for cyclohexene C=C bond.

Tosyl O1 atom does not depart from the phenyl ring plane. The O1—S1—C5 and O2—S1—C5 bond angles, as well as the O—S bond lengths are essentially equal as expected (Kelebekli *et al.*, 2006).

The closest Br···C intermolecular distance is 3.428 (6)Å with no hydrogen atom directed even approximately along this line, so the Br atoms do not participate in hydrogen bonds. In the crystal structure Br2 atoms are facing one another along the c-axis and the Br2···Br2 interatomic distance is 3.556Å within the van der Waals distance of 3.70 Å. C15—Br1···Pi(phenyl) noncovalent interactions contribute to the stability of the overall structure. The C-donor bond vectors are directed more closely towards the mid-point of an individual aromatic bond (Br1···C6=3.428, Br1···C7=3.458 Å) rather then the ring centroid (X) with Br1···X=3.440 (4)Å and C—Br···X=144.16 (16)°. Most important, the bromine does not coordinate to the benzene ring symmetrically in striking contrast to the coaxial (delocalized) model reported by Hassel & Stromme (1959). Instead, the bromine is positioned over the rim (not over the center) of the phenyl ring which corresponds to one of the highest electron density positions. Such experimental location of bromine is in good agreement with the data on noncovalent binding of halogens to aromatic donors (Vasilyev *et al.*, 2001).

In the crystal structure the adjacent phenyl moieties are stacked opposed to each other. The distance between ring centroids is 3.893 (5)Å and the corresponding slip angle is 7.4°. The crystal structure is also stabilized by two weak intermolecular hydrogen bonds (Fig. 3).

Experimental

For preparation of 6a and 6 b, to a stirred solution of diol (5a) and (5 b) (0.525 g, 2.05 mmol) in anhydrous THF (20 ml) under N_2 at room temperature *p*-toluensulfonyl isocyanate (0.8 g, 4.1 mmol= 0.62 ml) was added via syringe. The reaction was stirred at room temperature for 5 h and then the reaction temperature was increased to 335 K in 30 min. To another flask containing tris(dibenzylideneacetone)dipalladium chloroform complex (0.112 g, 108 µmol) in anhydrous THF (10 ml) under N_2 at room temperature triisopropylphosphite (0.40 g, 1.94 mmol) was added dropwise and stirred at room temperature for 30 min until a clear yellow color was obtained. The prepared catalyst mixture was added to the main reaction mixture and stirred at 335 K for 12 h. After removal of the solvent under reduced pressure (325 K, 20 m mH g), the residue was purified on a silica gel (60 g) by elution with 20% ethyl acetate / hexane to afford 6 b (70 mg, 7.2%). White crystals, mp 469-470 K (from hexane/ethyl acetate). ν_{max} (KBr); 3080, 3055, 3004, 2953, 1778, 1600, 1497, 1421, 1370, 1319, 1268, 1217, 1165, 1140, 1089, 1038 cm^{-1}; 1*H*-NMR (200 MHz $CDCl_3$ ppm) 7.94 (br d, A part of AA' BB' system, J= 8.3 Hz, 2H, aromatic), 7.34 (br d, B part of AA'BB' system, J= 8.3 Hz, 2H, aromatic), 6.11 (br s, 2H, -CH=CH), 4.93 (d, J= 7.3 Hz,1*H*, —CH—O), 4.80 (dd, J= 7.2, 2.0 Hz,1*H*, —CH—N), 4.37 and 4.33 (td, J= 6.5, 1.2 Hz, 2H —CH—Br), 3.62 (td, J=10.1, 2.1 Hz, 1H, —CH), 3.17 (dd, J= 6.9, 1.4 Hz, 1H, —CH), 2.47 (s, 3H, arom-CH_3); 13 C-NMR (50 MHz $CDCl_3$ ppm) δ 151.9 (C═O), 147.4 and 137.3 (ipso C$^{'}$s), 131.7, 130.6,130.4 and 125.0 (HC═CH and aromatic), 71.7 (C—O), 54.4 and 53.6 (—CH—Br), 45.1 and 43.7 (CH), 41.3 (—C—N), 23.7 (arom-CH_3).

Refinement

The H atoms were placed in geometrically idealized positions (C—H=0.93-0.98 Å) and treated as riding, with U_{iso}(H)=1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Figures

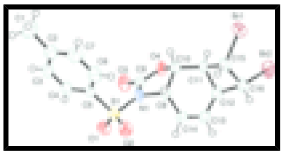
Fig. 1. The molecular structure of 6 b showing 50% probability displacement ellipsoids.

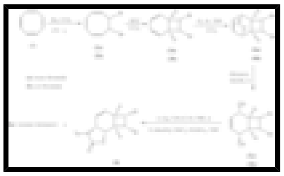
Fig. 2. Reaction scheme

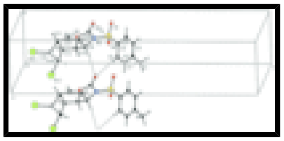
Fig. 3. The crystal structure of 6 b viewed down the a-axis. Hydrogen bonds are indicated by dashed lines.

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Crystal data

$C_{16}H_{15}Br_2NO_4S$

$M_r = 477.17$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 10.8513$ (4) Å

$b = 6.0019$ (3) Å

$c = 26.7246$ (7) Å

$\beta = 90.232$ (2)°

$V = 1740.52$ (12) Å^3

$Z = 4$

$F_{000} = 944$

$D_x = 1.821$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 6799 reflections

$\theta = 3.0$–30.5°

$\mu = 4.80$ mm^{-1}

$T = 293$ (2) K

Block, brown

0.32 × 0.21 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID S diffractometer

oscillation scans

Absorption correction: multi-scan
(Blessing, 1995)

$T_{min} = 0.310$, $T_{max} = 0.383$

44718 measured reflections

5328 independent reflections

4398 reflections with $I > 2\sigma(I)$

$R_{int} = 0.097$

$\theta_{max} = 30.6$°

$\theta_{min} = 3.0$°

$h = -15 \rightarrow 15$

$k = -8 \rightarrow 7$

$l = -38 \rightarrow 38$

Refinement

Refinement on F^2

$w = 1/[\sigma^2(F_o^2) + 4.0303P]$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.099$

$wR(F^2) = 0.144$

$S = 1.39$

5328 reflections

218 parameters

H-atom parameters constrained

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

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

$\Delta\rho_{max} = 0.62$ e Å^{-3}

$\Delta\rho_{min} = -0.48$ e Å^{-3}

Extinction correction: none

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.82396 (6)	−0.33398 (11)	0.35382 (2)	0.05280 (18)
Br2	0.97931 (7)	0.00899 (15)	0.43399 (2)	0.0734 (3)
N1	1.0135 (4)	0.2449 (8)	0.18456 (15)	0.0398 (10)
S1	1.08884 (13)	0.2442 (3)	0.13037 (5)	0.0441 (3)
O1	1.1277 (4)	0.4663 (8)	0.11961 (15)	0.0614 (12)
O2	1.1774 (4)	0.0710 (8)	0.13677 (14)	0.0600 (12)
O3	0.9097 (4)	0.5830 (7)	0.18095 (15)	0.0578 (11)
O4	0.8846 (3)	0.3462 (6)	0.24463 (12)	0.0435 (9)
C1	0.6963 (6)	−0.0249 (14)	−0.0174 (2)	0.078 (2)
H1A	0.618	0.0001	−0.0018	0.117*
H1B	0.7041	−0.1796	−0.0259	0.117*
H1C	0.7018	0.0637	−0.0472	0.117*
C2	0.7985 (5)	0.0399 (11)	0.0183 (2)	0.0515 (15)
C3	0.8497 (6)	0.2495 (12)	0.0169 (2)	0.0564 (16)
H3	0.8235	0.3501	−0.0074	0.068*
C4	0.9395 (5)	0.3134 (10)	0.0509 (2)	0.0497 (14)
H4	0.9733	0.4557	0.0496	0.06*
C5	0.9780 (5)	0.1634 (9)	0.08647 (17)	0.0392 (11)
C6	0.9301 (6)	−0.0502 (10)	0.0878 (2)	0.0506 (14)
H6	0.9588	−0.1528	0.1112	0.061*
C7	0.8398 (6)	−0.1090 (10)	0.0542 (2)	0.0528 (15)
H7	0.8058	−0.251	0.0556	0.063*
C8	0.9333 (5)	0.4099 (9)	0.20073 (19)	0.0418 (12)
C9	1.0333 (4)	0.0759 (9)	0.22463 (17)	0.0352 (10)
H9	1.0355	−0.0748	0.2106	0.042*
C10	0.9155 (4)	0.1127 (8)	0.25475 (17)	0.0347 (11)
H10	0.8498	0.0154	0.2421	0.042*
C11	0.9284 (5)	0.0853 (9)	0.31047 (17)	0.0364 (11)
H11	0.8567	0.1481	0.3277	0.044*

C12	1.0497 (5)	0.1659 (10)	0.33545 (18)	0.0431 (12)
H12	1.0403	0.3043	0.3545	0.052*
C13	1.1566 (5)	0.1682 (10)	0.3009 (2)	0.0484 (14)
H13	1.2336	0.2019	0.3143	0.058*
C14	1.1500 (5)	0.1263 (9)	0.2528 (2)	0.0426 (13)
H14	1.2232	0.1278	0.2348	0.051*
C15	0.9573 (5)	−0.1502 (9)	0.33031 (18)	0.0406 (12)
H15	1.004	−0.2323	0.305	0.049*
C16	1.0479 (5)	−0.0463 (10)	0.36853 (18)	0.0460 (13)
H16	1.1276	−0.1229	0.3698	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0580 (4)	0.0512 (3)	0.0492 (3)	−0.0040 (3)	0.0102 (2)	0.0088 (3)
Br2	0.0826 (5)	0.1077 (6)	0.0299 (3)	−0.0011 (4)	−0.0012 (3)	−0.0001 (3)
N1	0.046 (2)	0.042 (2)	0.031 (2)	0.002 (2)	0.0003 (17)	0.0067 (18)
S1	0.0397 (7)	0.0582 (9)	0.0345 (6)	−0.0040 (7)	0.0007 (5)	0.0086 (6)
O1	0.059 (3)	0.071 (3)	0.054 (2)	−0.029 (2)	−0.0044 (19)	0.014 (2)
O2	0.050 (2)	0.087 (3)	0.043 (2)	0.017 (2)	0.0068 (17)	0.009 (2)
O3	0.076 (3)	0.043 (2)	0.054 (2)	0.008 (2)	0.000 (2)	0.0120 (19)
O4	0.051 (2)	0.045 (2)	0.0344 (18)	0.0132 (18)	0.0006 (15)	0.0063 (16)
C1	0.065 (5)	0.111 (7)	0.056 (4)	−0.006 (4)	−0.011 (3)	−0.018 (4)
C2	0.047 (3)	0.065 (4)	0.042 (3)	0.004 (3)	0.003 (2)	−0.010 (3)
C3	0.061 (4)	0.072 (4)	0.036 (3)	0.003 (3)	−0.006 (3)	0.017 (3)
C4	0.056 (4)	0.051 (4)	0.042 (3)	−0.005 (3)	−0.002 (2)	0.013 (3)
C5	0.041 (3)	0.047 (3)	0.030 (2)	0.000 (2)	0.0018 (19)	0.004 (2)
C6	0.063 (4)	0.043 (3)	0.046 (3)	0.004 (3)	0.002 (3)	0.006 (3)
C7	0.060 (4)	0.039 (3)	0.059 (4)	−0.006 (3)	0.001 (3)	−0.011 (3)
C8	0.049 (3)	0.040 (3)	0.037 (3)	0.002 (2)	−0.007 (2)	0.004 (2)
C9	0.041 (3)	0.034 (3)	0.031 (2)	0.000 (2)	−0.0027 (19)	0.0070 (19)
C10	0.036 (3)	0.038 (3)	0.031 (2)	0.002 (2)	−0.0020 (19)	0.003 (2)
C11	0.039 (3)	0.042 (3)	0.028 (2)	0.007 (2)	−0.0011 (19)	0.004 (2)
C12	0.052 (3)	0.044 (3)	0.033 (2)	−0.001 (3)	−0.011 (2)	0.000 (2)
C13	0.041 (3)	0.057 (4)	0.047 (3)	−0.013 (3)	−0.013 (2)	0.011 (3)
C14	0.032 (3)	0.052 (4)	0.044 (3)	−0.004 (2)	−0.003 (2)	0.011 (2)
C15	0.045 (3)	0.044 (3)	0.033 (2)	0.006 (2)	0.006 (2)	0.006 (2)
C16	0.044 (3)	0.063 (4)	0.031 (2)	0.012 (3)	−0.001 (2)	0.010 (2)

Geometric parameters (Å, °)

Br1—C15	1.926 (5)	C6—H6	0.93
Br2—C16	1.933 (5)	C14—C13	1.310 (7)
S1—O2	1.425 (4)	C14—H14	0.93
S1—O1	1.428 (4)	C10—C11	1.504 (6)
S1—N1	1.666 (4)	C10—H10	0.98
S1—C5	1.746 (5)	C4—C3	1.383 (8)
O4—C8	1.344 (6)	C4—H4	0.93
O4—C10	1.466 (6)	C11—C15	1.542 (7)

O3—C8	1.193 (6)	C11—H11	0.98
N1—C8	1.388 (7)	C13—H13	0.93
N1—C9	1.490 (6)	C2—C3	1.376 (9)
C5—C4	1.373 (7)	C2—C7	1.384 (8)
C5—C6	1.384 (8)	C2—C1	1.511 (8)
C9—C14	1.501 (7)	C7—H7	0.93
C9—C10	1.530 (7)	C15—C16	1.546 (7)
C9—H9	0.98	C15—H15	0.98
C12—C13	1.486 (8)	C3—H3	0.93
C12—C16	1.550 (7)	C16—H16	0.98
C12—C11	1.551 (7)	C1—H1A	0.96
C12—H12	0.98	C1—H1B	0.96
C6—C7	1.372 (8)	C1—H1C	0.96

O2—S1—O1	120.4 (3)	C10—C11—C15	117.3 (4)
O2—S1—N1	103.3 (2)	C10—C11—C12	117.9 (4)
O1—S1—N1	108.6 (3)	C15—C11—C12	88.1 (4)
O2—S1—C5	109.9 (3)	C10—C11—H11	110.6
O1—S1—C5	109.1 (3)	C15—C11—H11	110.6
N1—S1—C5	104.2 (2)	C12—C11—H11	110.6
C8—O4—C10	110.0 (4)	O3—C8—O4	123.3 (5)
C8—N1—C9	110.5 (4)	O3—C8—N1	128.1 (5)
C8—N1—S1	125.6 (4)	O4—C8—N1	108.5 (4)
C9—N1—S1	123.6 (3)	C14—C13—C12	124.7 (5)
C4—C5—C6	120.8 (5)	C14—C13—H13	117.7
C4—C5—S1	119.4 (4)	C12—C13—H13	117.7
C6—C5—S1	119.8 (4)	C3—C2—C7	118.6 (5)
N1—C9—C14	110.0 (4)	C3—C2—C1	120.9 (6)
N1—C9—C10	99.3 (4)	C7—C2—C1	120.4 (6)
C14—C9—C10	114.3 (4)	C6—C7—C2	121.1 (6)
N1—C9—H9	110.9	C6—C7—H7	119.5
C14—C9—H9	110.9	C2—C7—H7	119.5
C10—C9—H9	110.9	C11—C15—C16	89.2 (4)
C13—C12—C16	112.0 (5)	C11—C15—Br1	119.0 (4)
C13—C12—C11	113.5 (4)	C16—C15—Br1	119.5 (3)
C16—C12—C11	88.7 (4)	C11—C15—H15	109.2
C13—C12—H12	113.5	C16—C15—H15	109.2
C16—C12—H12	113.5	Br1—C15—H15	109.2
C11—C12—H12	113.5	C2—C3—C4	121.3 (6)
C7—C6—C5	119.2 (5)	C2—C3—H3	119.4
C7—C6—H6	120.4	C4—C3—H3	119.4
C5—C6—H6	120.4	C15—C16—C12	87.9 (4)
C13—C14—C9	124.9 (5)	C15—C16—Br2	114.9 (4)
C13—C14—H14	117.5	C12—C16—Br2	112.4 (4)
C9—C14—H14	117.5	C15—C16—H16	113.1
O4—C10—C11	107.9 (4)	C12—C16—H16	113.1
O4—C10—C9	103.4 (4)	Br2—C16—H16	113.1
C11—C10—C9	115.5 (4)	C2—C1—H1A	109.5
O4—C10—H10	109.9	C2—C1—H1B	109.5
C11—C10—H10	109.9	H1A—C1—H1B	109.5

C9—C10—H10	109.9	C2—C1—H1C	109.5
C5—C4—C3	119.0 (6)	H1A—C1—H1C	109.5
C5—C4—H4	120.5	H1B—C1—H1C	109.5
C3—C4—H4	120.5		

O2—S1—N1—C8	167.3 (4)	C13—C12—C11—C10	−25.2 (7)
O1—S1—N1—C8	38.4 (5)	C16—C12—C11—C10	−138.7 (5)
C5—S1—N1—C8	−77.8 (5)	C13—C12—C11—C15	94.9 (5)
O2—S1—N1—C9	−6.5 (5)	C16—C12—C11—C15	−18.6 (4)
O1—S1—N1—C9	−135.4 (4)	C10—O4—C8—O3	170.7 (5)
C5—S1—N1—C9	108.4 (4)	C10—O4—C8—N1	−10.2 (6)
O2—S1—C5—C4	−136.8 (4)	C9—N1—C8—O3	169.7 (5)
O1—S1—C5—C4	−2.8 (5)	S1—N1—C8—O3	−4.8 (9)
N1—S1—C5—C4	113.1 (5)	C9—N1—C8—O4	−9.3 (6)
O2—S1—C5—C6	43.1 (5)	S1—N1—C8—O4	176.2 (4)
O1—S1—C5—C6	177.1 (4)	C9—C14—C13—C12	1.9 (10)
N1—S1—C5—C6	−67.0 (5)	C16—C12—C13—C14	104.2 (6)
C8—N1—C9—C14	−97.1 (5)	C11—C12—C13—C14	5.7 (8)
S1—N1—C9—C14	77.5 (5)	C5—C6—C7—C2	1.8 (9)
C8—N1—C9—C10	23.2 (5)	C3—C2—C7—C6	−0.1 (9)
S1—N1—C9—C10	−162.2 (4)	C1—C2—C7—C6	−178.1 (6)
C4—C5—C6—C7	−2.4 (8)	C10—C11—C15—C16	139.2 (4)
S1—C5—C6—C7	177.7 (4)	C12—C11—C15—C16	18.6 (4)
N1—C9—C14—C13	120.0 (6)	C10—C11—C15—Br1	−97.1 (5)
C10—C9—C14—C13	9.3 (8)	C12—C11—C15—Br1	142.3 (4)
C8—O4—C10—C11	147.6 (4)	C7—C2—C3—C4	−0.9 (9)
C8—O4—C10—C9	24.7 (5)	C1—C2—C3—C4	177.1 (6)
N1—C9—C10—O4	−27.3 (4)	C5—C4—C3—C2	0.3 (9)
C14—C9—C10—O4	89.8 (5)	C11—C15—C16—C12	−18.6 (4)
N1—C9—C10—C11	−144.9 (4)	Br1—C15—C16—C12	−141.9 (4)
C14—C9—C10—C11	−27.9 (6)	C11—C15—C16—Br2	95.2 (4)
C6—C5—C4—C3	1.4 (9)	Br1—C15—C16—Br2	−28.2 (6)
S1—C5—C4—C3	−178.7 (4)	C13—C12—C16—C15	−96.3 (5)
O4—C10—C11—C15	178.3 (4)	C11—C12—C16—C15	18.5 (4)
C9—C10—C11—C15	−66.6 (6)	C13—C12—C16—Br2	147.5 (4)
O4—C10—C11—C12	−78.4 (5)	C11—C12—C16—Br2	−97.6 (4)
C9—C10—C11—C12	36.7 (6)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O3^{i}	0.93	2.51	3.331 (7)	148
C9—H9···O3^{i}	0.98	2.59	3.450 (7)	147

Symmetry codes: (i) *x*, *y*−1, *z*.

Fig. 1

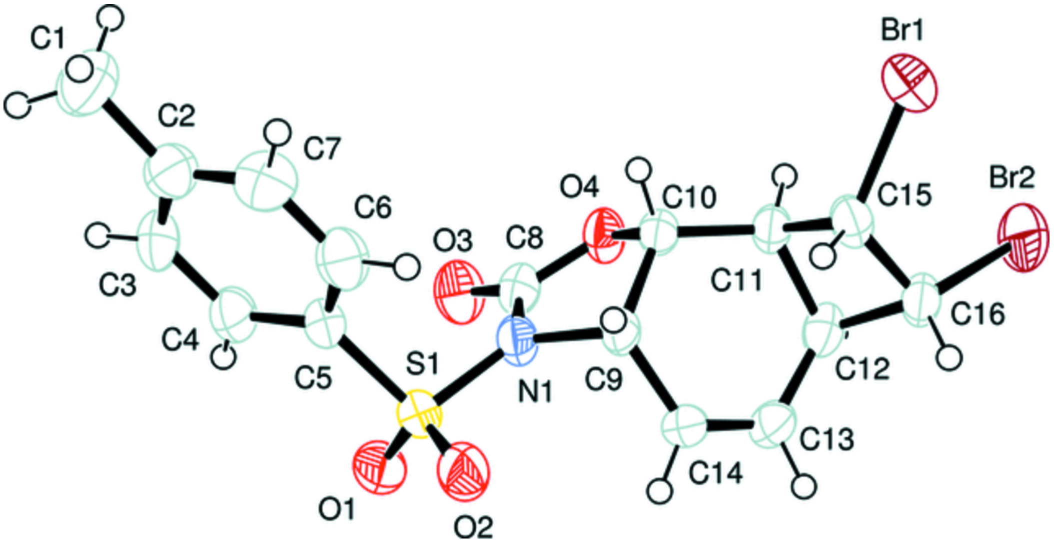

C1
C2
C7
C6
C3
C4
C5
O3
C8
O4
S1
N1
C9
O1
O2
C10
C11
C14
C13
C12
C15
C16
Br1
Br2

Fig. 2

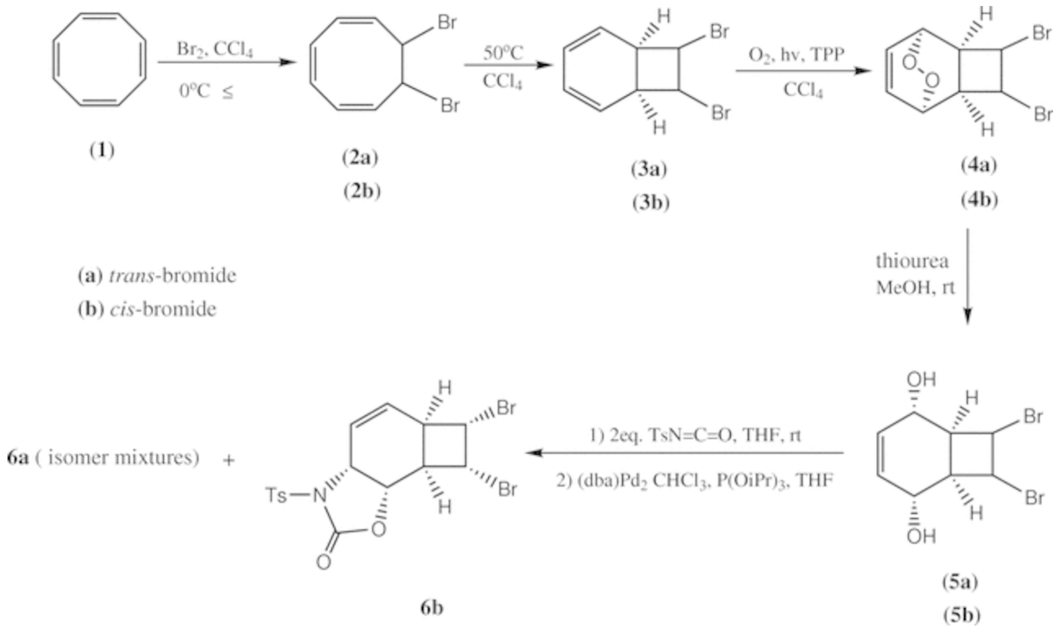
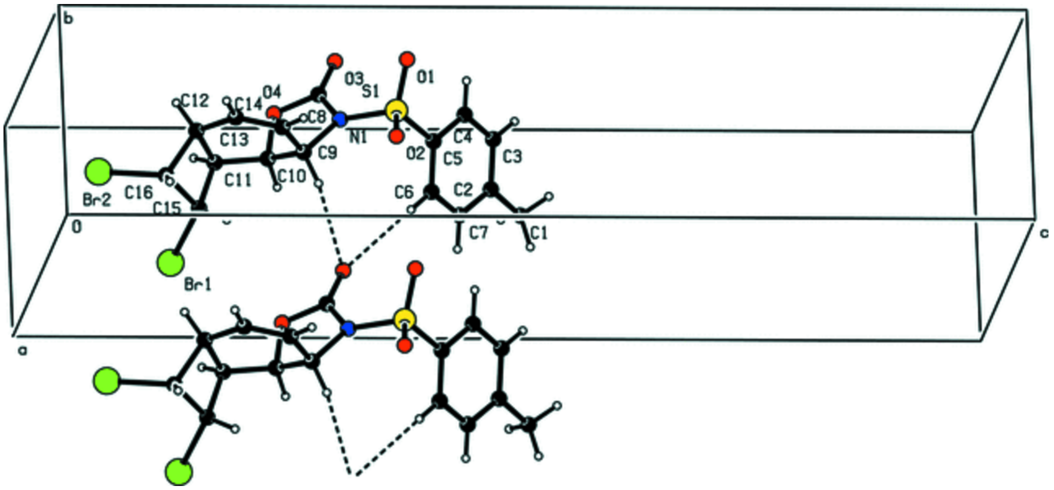

(1)
Br2, CCl4
0°C ≤
(2a)
(2b)
50°C
CCl4
(3a)
(3b)
O2, hv, TPP
CCl4
(4a)
(4b)
thiourea
MeOH, rt
(a) trans-bromide
(b) cis-bromide
(5a)
(5b)
1) 2eq. TsN=C=O, THF, rt
2) (dba)Pd2 CHCl3, P(OiPr)3, THF
6a (isomer mixtures) +
6b
Br
H
OH
Ts
N
O

Fig. 3


b
O3
S1
O1
C12
C14
O4
C8
N1
C13
C9
O2
C4
C5
C3
C11
C10
Br2
C16
C6
C2
C15
0
C7
C1
c
Br1
a