Crystal structures of two bicyclo[5.1.0]octanes: potassium *trans*-bicyclo[5.1.0]octane-4-carboxylate monohydrate and *cis*-bicyclo[5.1.0]octan-4-yl 4-bromobenzenesulfonate

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The crystal structures of the *trans*-fused compound potassium *trans*-bicyclo[5.1.0]octane-4-carboxylate monohydrate, $K^+ \cdot C_9H_{13}O_2{}^- \cdot H_2O$, (I), and of *cis*-bicyclo[5.1.0]octan-4-yl 4-bromobenzenesulfonate, $C_{14}H_{17}BrO_3S$, (II), have been determined. Compound (I) represents the smallest *trans*-fused cyclopropane structure known to date, and features the expected *shortening* of the bridging C—C bond relative to the other cyclopropane bond lengths, in contrast to the *cis*-fused system, (II), where all of the cyclopropane bond lengths are the same. The bicyclic ring system of (I) is disordered across a crystallographic mirror plane. The geometries of the *cis*-fused and *trans*-fused ring systems are compared.

1. Chemical context

Extensive studies on the reactivities of the bridge bond in *trans*-fused bicyclic cyclopropane derivatives (Gassman *et al.*, 1968) led to proposal of the 'twist'-bent bond to describe the bonding in these [5.1.0] bicyclic systems (Gassman, 1967). The [5.1.0]octanes are expected to be more highly strained than the corresponding *trans*-fused bicyclo[4.2.0]octanes which had previously been prepared (Cava & Moroz, 1962). Our studies were initiated in order to illuminate discussions of bonding by providing accurate geometric parameters for the most strained systems available. Several 4-substituted derivatives of *trans*-fused bicyclic [5.1.0]octanes were studied, but in most, disordering of the molecules in the crystal precluded any refined structure that would give useful information. Even the *trans*-fused bicyclic [5.1.0]octane 4-carboxylate structure presented here is disordered, but we were able to determine a reasonable geometry for the bicyclic system. The structure of a 4-substituted *cis*-fused bicyclic [5.1.0]octane was also determined, so that a comparison of the ring geometries could be made. These studies formed part of the MS and PhD theses of one of us (Kershaw, 1972, 1974), and were presented at the 1973 winter meeting of The American Crystallographic Association.

2. Structural commentary

Table 1 presents a comparison of the geometries of the *trans*-fused [5.1.0] (I) and *cis*-fused [5.1.0] (II) octane rings. Figs. 1 and 2 show the asymmetric units of the two molecules, while Figs. 3 and 4 show the *cis*- and *trans*-fused rings superimposed upon one another. It can be seen that in the *cis*-fused system (II), chemically equivalent bonds and angles are the same, and
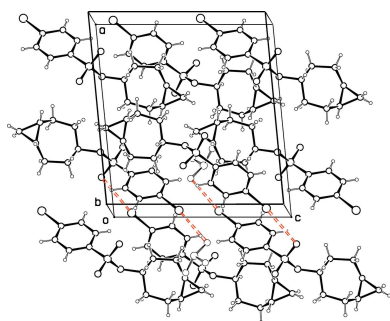
so are the torsional angles. Thus the *cis*-fused compound has an excellent, non-crystallographic molecular mirror plane.

(I)

(II)
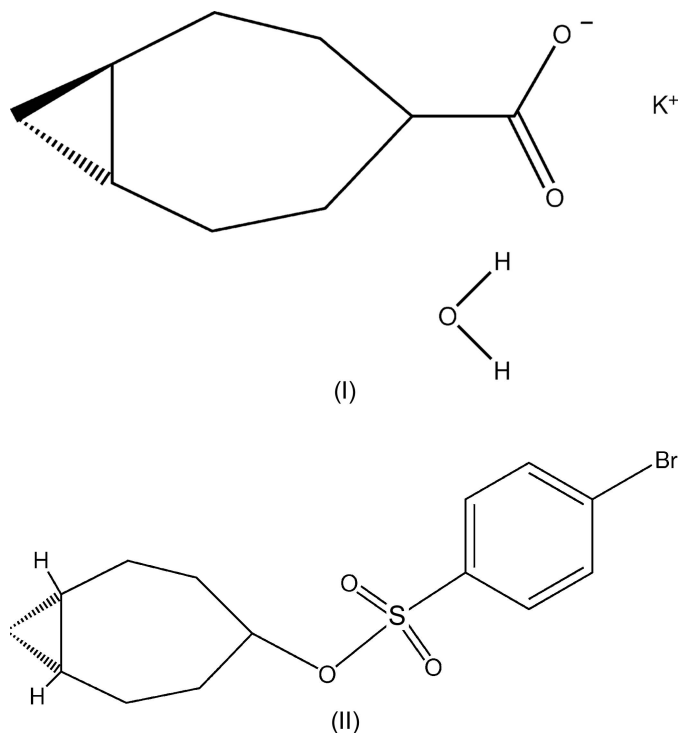
In contrast, while the *trans*-fused derivative cannot have a molecular mirror plane; the molecule sits astride a crystallographic mirror plane, probably due to the packing requirements of the potassium cation and the carboxylate part of the molecule, and necessarily leading to a disordered structure. Treatment of the disorder is discussed in the *Refinement* section. One of the assumptions made in the refinements of (I) was that chemically equivalent bonds and angles would be the
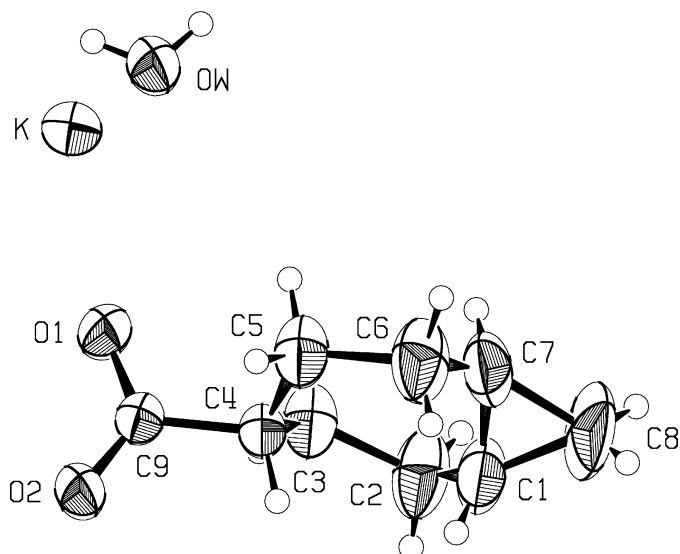

Figure 1
The asymmetric unit of compound (I). Displacement ellipsoids are at the 50% probability level. Sizes of the H atoms are arbitrary.
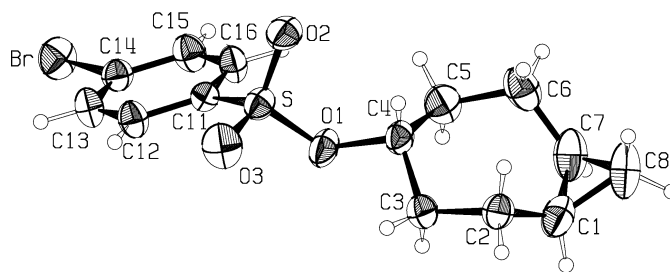

Figure 2
The asymmetric unit of compound (II). Displacement ellipsoids are at the 50% probability level. Sizes of the H atoms are arbitrary.

same, so it was important to verify that this was the case in the *cis*-fused compound, (II). In both structures, the substituent on C4 is in the *exo* position. In (I), the plane of the carboxylate substituent on C4 is necessarily at 90° to the molecular plane through C2, C3, C5 and C6, while in (II) the roughly planar set C4, O1, S and C11 is tilted at 71.9 (2)° to the molecular plane and at 49.6 (1)° to the plane through the phenyl group. In both structures, displacement ellipsoids for the cyclopropane methylene group indicate motion perpendicular to the cyclopropane ring.

The two bicyclic systems are rather similar in the top view given in Fig. 3. *trans*-Fusion changes the conformation angles around C2—C3 and C5—C6, as seen in Fig. 4 and in Table 1.
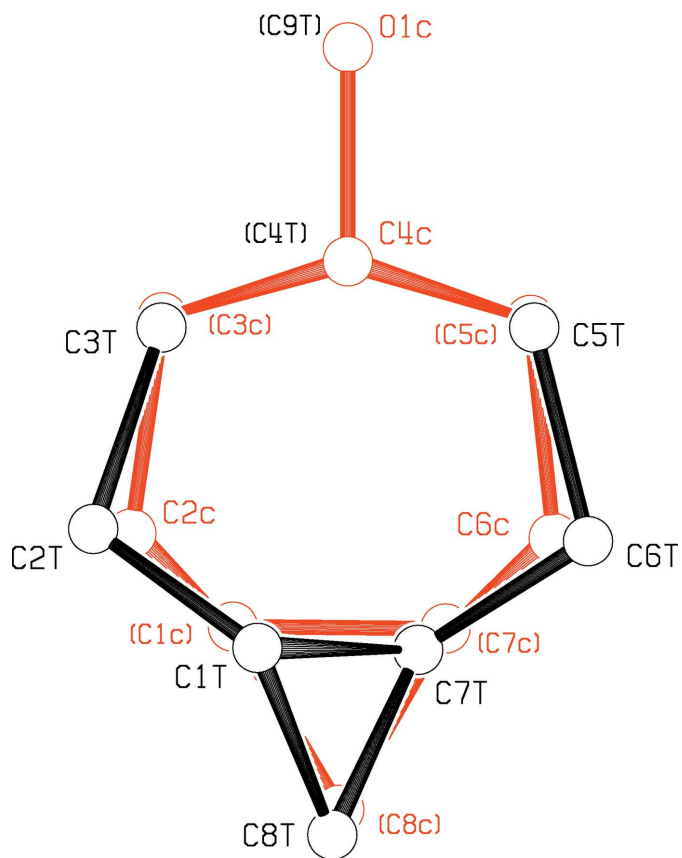

Figure 3
A superposition of the ring systems found for (I) and (II), viewed normal to the planes through C3, C4 and C5. The *trans*-fused structure is in black and the *cis*-fused structure in red.

Table 1
Selected bond lengths, angles, and conformational angles (Å, °), for (I) and (II).

|	(I) (trans)	(II) (cis)		(I) (trans)	(II) (cis)
C1—C2	1.513 (4)	1.485 (4)	C7—C1—C2	112.9 (5)	119.5 (3)
C6—C7	1.514 (4)	1.502 (5)	C6—C7—C1	112.8 (5)	119.6 (3)
C2—C3	1.543 (4)	1.534 (3)	C1—C2—C3	107.1 (3)	112.9 (2)
C5—C6	1.543 (3)	1.542 (4)	C5—C6—C7	107.1 (3)	113.3 (3)
C3—C4	1.538 (3)	1.510 (4)	C2—C3—C4	117.8 (6)	113.1 (2)
C5—C4	1.538 (4)	1.500 (4)	C6—C5—C4	117.2 (4)	112.2 (2)
			C3—C4—C5	118.0 (3)	118.5 (2)
			C2—C1—C8	130.5 (4)	121.6 (3)
			C6—C7—C8	130.4 (4)	120.9 (3)
C1—C8	1.500 (4)	1.499 (5)	C7—C1—C8	60.82 (14)	59.7 (2)
C7—C8	1.500 (4)	1.489 (5)	C1—C7—C8	60.80 (14)	60.3 (2)
C1—C7	1.463 (6)	1.493 (5)	C1—C8—C7	58.4 (3)	60.0 (2)
			C1—C2—C3—C4	−28.1 (12)	−81.7 (3)
			C7—C6—C5—C4	46.4 (12)	80.7 (4)
			C2—C3—C4—C5	82.2 (8)	64.4 (3)
			C6—C5—C4—C3	−66.4 (8)	−63.4 (4)
			C3—C2—C1—C7	−53.6 (9)	66.1 (4)
			C5—C6—C7—C1	−75.1 (8)	−67.2 (4)
			C2—C1—C7—C6	110.5 (5)	0.6 (5)
			C2—C1—C7—C8	−124.8 (3)	111.6 (4)
			C6—C7—C1—C8	−124.8 (3)	−110.9 (4)
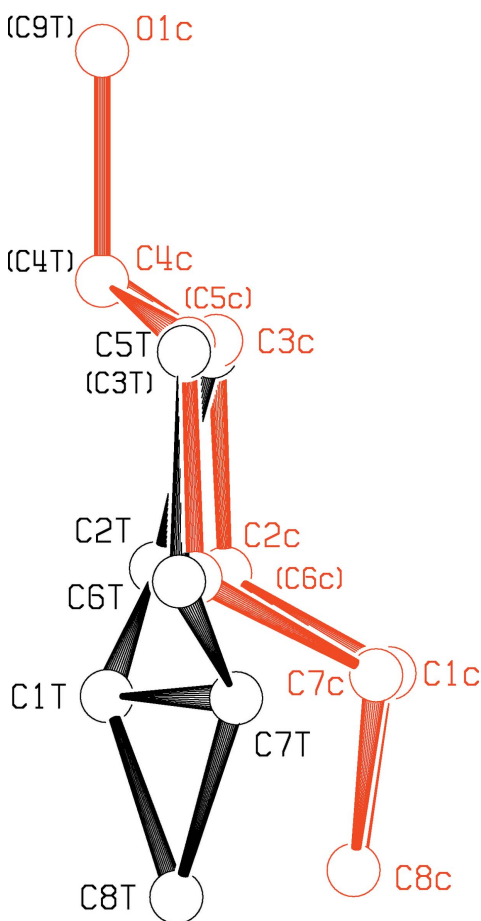
Figure 4
A view of the superposition of (I) and (II) at 90° to that in Fig. 3.

Fig. 3 shows that the *trans*-fusion is also accommodated by expansion of the angles at C3 and C5 from an average of 112.7 (2) to 117.5 (8)°, contraction of the angles at C2 and C6 from an average of 113.1 (3) to 107.1 (4)°, an increase in the external angles at C1 and C7 to 130.4 (8) from an average of 121.3 (3)°, and a lengthening of bonds C3—C4 and C5—C4 from 1.505 (4) to 1.538 (4) Å. The H1···H7 distance of 2.32 Å in (II) is increased to 2.84 Å in the *trans*-fused (I) structure. There is a significant shortening of the bridgehead bond C1—C7 in the *trans*-fused compound, from 1.493 (5) Å in (II) to 1.463 (6) Å in (I), which leads to a distortion of the cyclopropane ring from equilateral triangular geometry, with reduction of the angle at C8 from 60.0 (2)° in (II) to 58.4 (3)° in (I). Such shortening of the strained twist-bent bond, though counter-intuitive, was expected (Kershaw, 1974, p2), because much of the electron density of the bond would lie outside the internuclear line. We carried out geometry optimization of both *trans*- and *cis*-fused C_8H_{14} systems using B3LYP density functional calculations (*GAUSSIAN09*; Frisch *et al.*, 2013), with results that also showed the trends noted above, including a calculated shortening of the bridgehead C1—C7 bond length by 0.014 Å.

3. Supramolecular features

Fig. 5 gives a packing diagram for (I). There are alternating layers of hydrophobic interactions between the cyclopropane ends of the molecules and of charge interactions between the carboxylate ends of the molecules and the potassium ions. In addition, the water molecules in (I) form strong hydrogen

Table 2
Hydrogen-bond geometry (Å, °) for (I).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$OW—HWA \cdots O1^i$	0.82 (1)	1.88 (1)	2.701 (3)	180 (4)
$OW—HWB \cdots O2^{ii}$	0.82 (1)	2.08 (3)	2.757 (4)	140 (3)

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

bonds (Table 2) to carboxylate oxygen atoms of two separate [5.1.0] octane molecules, linking the anions into chains parallel to the *b* axis, as can be seen in Fig. 6. The hydrogen-bond lengths are rather short, with $O3—H \cdots O1(x - \frac{1}{2}, 1 - y, z) = 2.701$ (3) Å and $O3—H \cdots O2(x - 1, y, z) = 2.757$ (4) Å. The water O atoms may lie slightly off the mirror plane at $y = 1/4$, as indicated by the displacement ellipsoid values, which would change the hydrogen-bond geometry a little. Strong hydrogen
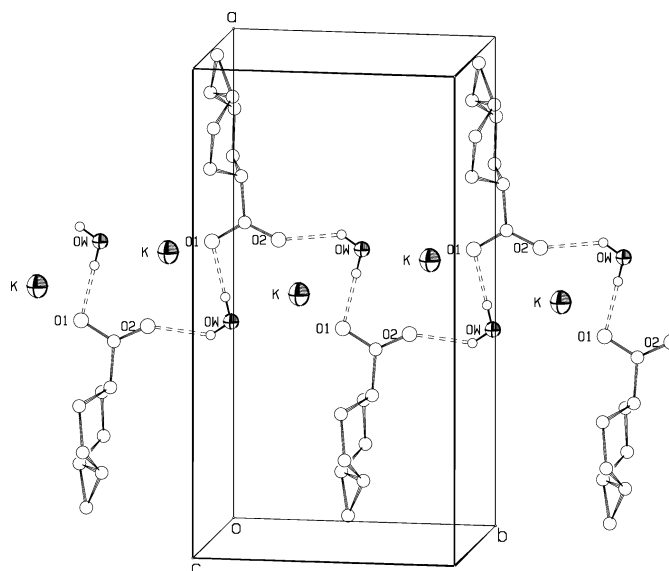
Figure 6
One of the two hydrogen-bonded chains parallel to the *b* axis in (I).

bonds are consistent with retention of the water of hydration even after recrystallization from a non-aqueous solvent, and also with the shifts in O—H stretching frequencies in the IR to 3060 and 3360 cm^{-1}. The potassium ions lie in between two of the hydrogen-bonded chains, and have four carboxylate and two water oxygen atoms as near neighbors, in a distorted flattened trigonal–prismatic array, with K—O distances ranging from 2.719 (3) to 2.879 (3) Å.

The supramolecular structure for (II) features the presence of intermolecular halogen bonds between Br and O2 (Fig. 7), which link molecules related by the screw axes at $x = 0$ into a helical arrangement. The $Br \cdots O2(2 - x, y - 1/2, -z - 1/2)$ distance is 3.230 (2) Å, which is 96% of the sum of the van der Waals radii, while the $C14—Br \cdots O2$ and $Br \cdots O2—C9$

Figure 5
Projection of (I) down the *b* axis. Disordered [5.1.0]octane moieties related by the mirror at $z = 0.25$ are not shown.
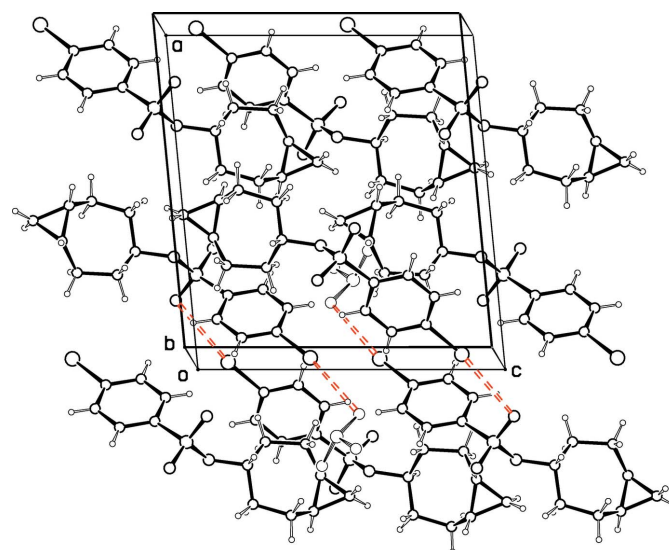
Figure 7
Packing diagram for (II), showing halogen bonds in red.

Table 3
Experimental details.

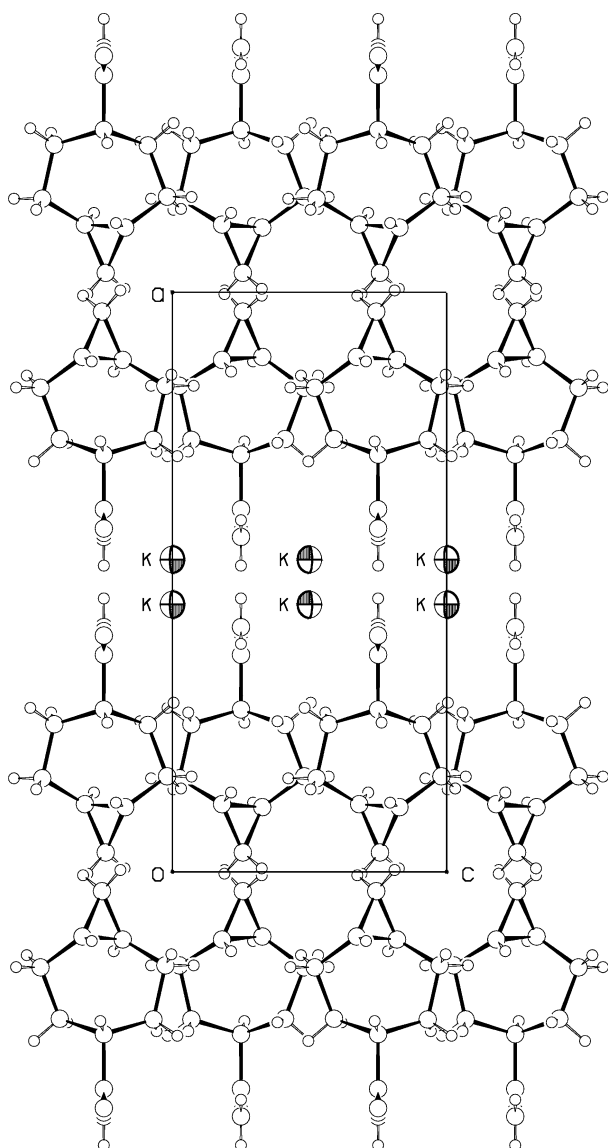|	(I)	(II)
Crystal data		
Chemical formula	$K^+\cdot C_9H_{13}O_2{}^-\cdot H_2O$	$C_{14}H_{17}BrO_3S$
M_r	210.31	345.24
Crystal system, space group	Orthorhombic, $Pbcm$	Monoclinic, $P2_1/c$
Temperature (K)	297	297
a, b, c (Å)	16.148 (13), 8.631 (9), 7.674 (10)	12.829 (1), 9.759 (1), 11.730 (2)
α, β, γ (°)	90, 90, 90	90, 95.74 (1), 90
V (Å^3)	1070 (2)	1461.2 (3)
Z	4	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.47	5.19
Crystal size (mm)	$0.5 \times 0.4 \times 0.1$	$0.29 \times 0.24 \times 0.18$
Data collection		
Diffractometer	Picker four-circle	Picker four-circle
Absorption correction	Gaussian (Busing & Levy, 1957)	Gaussian (Busing & Levy, 1957)
T_{min}, T_{max}	0.842, 0.954	0.267, 0.456
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	1926, 1104, 795	2447, 2381, 2154
R_{int}	0.02	0.02
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.735	0.580
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.096, 1.00	0.027, 0.091, 1.08
No. of reflections	1104	2381
No. of parameters	98	173
No. of restraints	16	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.15, −0.17	0.34, −0.31

Data reduction followed procedures in Corfield *et al.* (1973), with p = 0.05 for (I) and 0.06 for (II). Computer programs: *SHELXL2014* (Sheldrick, 2015), *ORTEPII* (Burnett & Johnson, 1996) and local superposition program (Corfield, 1972).

angles are 170.06 (8) and 107.81 (9)°, respectively. These parameters are consistent with moderate halogen bonding according to a systematic study of such intermolecular interactions in the CSD (Lommerse *et al.*, 1996). Also, a review of the role of halogen bonding in crystal engineering (Metrangolo *et al.*, 2005), stresses the importance in halogen bonding of the aromatically bound bromine seen in the present compound. There are no other intermolecular contacts of note and the shortest H···H contact is H3A ··· H8B($x, \frac{1}{2} - y, z - \frac{1}{2}$), at 2.47 Å.

4. Database survey

Of 399 hits in the Cambridge Structure Database (CSD, Version 5.35; Groom *et al.*, 2016) for the [5.1.0] ring system, 105 have 3D coordinates available, unsubstituted H atoms at the bridgehead positions, and conventional R factors of 0.05 or less, leading to 244 [5.1.0] geometries. All of the systems are *cis*-fused; no *trans*-fused [5.1.0] system was found. The average geometry of the CSD bicyclic ring systems displays the same near-perfect mirror symmetry found in the present *cis*-fused structure. The geometrical parameters of the *cis*-fused system described here do not differ significantly from the database geometries. In particular, the average bridgehead C—C bond length in the CSD set does not differ significantly from the other cyclopropane bond lengths, just as in the present *cis*-fused structure, (II), and in contrast to the *trans*-fused struc-

ture, (I), where the bridgehead C—C bond length is shortened. Both the current *cis*-structure and the ensemble of [5.1.0] structures show the significant lengthening of bonds C2—C3 and C5—C6 relative to other bonds in the ring system noted in Table 1.

Searches for simple bicyclic [6.1.0] systems yielded only 14 hits. Two of these were *trans*-fused structures, (Szabo *et al.*, 1973; Hayes *et al.*, 2005), with H1···H7 distances of 2.80 and 2.95 Å, respectively. In both structures, the bridgehead C—C bond length was longer by 0.03 Å than the other two cyclopropane C—C bond lengths, in contrast to the shorter bridgehead C—C bond observed in (I).

5. Synthesis and crystallization

Syntheses of these ring systems are described in Gassman *et al.* (1971). Samples of *trans*-fused bicyclo [5.1.0] octane 4-carboxylic acid and crystals of the *cis*-bicyclo[5.1.0]octan-4-yl 4-bromobenzenesulfonate were supplied by Dr Paul G. Gassman. The *trans*-fused acid was titrated with potassium hydroxide, and crystals of the potassium salt were obtained by evaporation to dryness and recrystallization from a benzene–methanol mixture. Analysis: C 50.89%, H 7.15%, in good agreement with calculated values of C 51.40% and H 7.19% for $K[C_9O_2H_{13}]\cdot H_2O$.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. For the *trans*-fused structure (I), only one octant of data was collected. Also in (I), reflections with $I<2\sigma$ were not saved when the data were processed. These weak reflections were later patched back into the structure factor file, with intensities set at $\sigma(I)$, where $\sigma(I)$ was the average value for reflections at a similar θ value for weak reflections in the data set with $2\sigma<I<3\sigma$. It became apparent, however, that most of the missing reflections were higher order. We chose to use a cut-off value of 0.82 for the resolution of reflections used in final refinements, as about 50% of the intensities at this resolution were above 3σ, while only 11% of the reflections at resolutions above this value had $I>2\sigma$.

After extensive efforts, it was concluded that the near-perfect mirror symmetry in (I) apart from C1 and C7 hampered successful refinement in the non-centrosymmetric space group $Pca2_1$. Accordingly, all further refinements were carried out assuming a disordered structure in space group $Pbcm$. Initially, only atoms C1 and C7 were disordered, but it became apparent that bonded atoms C2 and C6 should be refined individually, and that C8 should also be allowed to move off the mirror plane at $z = 0.25$. Later, atoms C3 and C5 were also refined individually. It was necessary to impose tight restraints on the geometry to overcome the high correlation between parameters for C2 and C3 and the reflected images of C5 and C6. This was done by tightly restricting differences between chemically equivalent bond lengths and angles on either side of the octane ring.

No special measures were necessary in the refinement of (II).

In both compounds, C-bound H atoms were constrained to idealized positions, with C—H distances of 0.97 Å for CH_2 groups, 0.98 Å for methine CH groups and 0.93 Å for aromatic H atoms, and with U_{eq} values set at 1.3 times the U_{iso} of their bonded atoms for the CH_2 H atoms, and 1.2 times for methine and aromatic H atoms. In (I), H1 and H7 were initially refined independently, in case their positions could throw light on the twist-bent bond, but as they refined into positions indistinguishable from the constrained positions, they were constrained in the final refinements. The water H atoms in (I) were found in a difference-Fourier map, and their positional coordinates were refined whilst their U_{eq} values set at 1.3 times the U_{iso} of the O atom. As a check, the U_{eq} values for these H atoms were allowed to vary, but as there was no appreciable change in these U values, they were constrained in the final refinement.

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supporting information

Crystal structures of two bicyclo[5.1.0]octanes: potassium *trans*-bicyclo-[5.1.0]octane-4-carboxylate monohydrate and *cis*-bicyclo[5.1.0]octan-4-yl 4-bromobenzenesulfonate

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Computing details

For both structures, data collection: Corfield (1972); cell refinement: Corfield (1972). Data reduction: Data reduction followed procedures in Corfield *et al.* (1973), with p = 0.05 for (I); Data reduction followed procedures in Corfield *et al.* (1973), with P = 0.06 for (II). For both structures, program(s) used to solve structure: local superposition program (Corfield, 1972); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

Potassium *trans*-bicyclo[5.1.0]octane-4-carboxylate monohydrate (I)

Crystal data

$K^+ \cdot C_9H_{13}O_2^- \cdot H_2O$	D_x = 1.306 Mg m^{-3}
M_r = 210.31	D_m = 1.345 (11) Mg m^{-3}
Orthorhombic, *Pbcm*	D_m measured by Flotation in benzene–carbon
a = 16.148 (13) Å	tetrachloride mixtures
b = 8.631 (9) Å	Mo $K\alpha$ radiation, λ = 0.7107 Å
c = 7.674 (10) Å	Cell parameters from 19 reflections
V = 1070 (2) Å^3	μ = 0.47 mm^{-1}
Z = 4	T = 297 K
$F(000)$ = 448	Plate, colorless
	0.5 × 0.4 × 0.1 mm

Data collection

Picker four-circle diffractometer	1104 independent reflections
Radiation source: sealed X-ray tube	795 reflections with $I > 2\sigma(I)$
Oriented graphite 200 reflection monochromator	R_{int} = 0.02
$\theta/2\theta$ scans	θ_{max} = 31.5°, θ_{min} = 1.3°
Absorption correction: gaussian Busing & Levy (1957)	h = 0→23
	k = 0→12
	l = 0→11
T_{min} = 0.842, T_{max} = 0.954	9 standard reflections every 220 reflections
1926 measured reflections	intensity decay: −3.0(8)

Refinement

Refinement on F^2	$wR(F^2)$ = 0.096
Least-squares matrix: full	S = 1.00
$R[F^2 > 2\sigma(F^2)]$ = 0.034	1104 reflections

98 parameters
16 restraints
Primary atom site location: heavy-atom method
Secondary atom site location: real-space vector
  search
Hydrogen site location: mixed

H atoms treated by a mixture of independent
  and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 0.250P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
K1	0.46108 (4)	0.2500	0.5000	0.0513 (2)	
OW	0.42215 (13)	0.4712 (2)	0.7500	0.0625 (6)	
HWA	0.4717 (8)	0.493 (4)	0.7500	0.081*	
HWB	0.3937 (19)	0.550 (3)	0.7500	0.081*	
O1	0.41518 (12)	0.0440 (2)	0.7500	0.0581 (6)	
O2	0.40765 (12)	−0.2105 (2)	0.7500	0.0603 (6)	
C1	0.1115 (2)	−0.0466 (5)	0.8279 (6)	0.0760 (17)	0.5
H1	0.1194	−0.1551	0.7941	0.091*	0.5
C2	0.1648 (4)	0.0018 (15)	0.9808 (6)	0.0853 (9)	0.5
H2A	0.1645	−0.0781	1.0697	0.111*	0.5
H2B	0.1439	0.0970	1.0315	0.111*	0.5
C3	0.2534 (3)	0.0263 (16)	0.9108 (9)	0.0640 (19)	0.5
H3A	0.2597	0.1353	0.8830	0.083*	0.5
H3B	0.2918	0.0032	1.0044	0.083*	0.5
C4	0.28013 (16)	−0.0677 (3)	0.7500	0.0449 (7)	
H4	0.2575	−0.1725	0.7626	0.054*	0.5
C5	0.2547 (3)	−0.0071 (16)	0.5693 (8)	0.0640 (19)	0.5
H5A	0.2829	−0.0691	0.4821	0.083*	0.5
H5B	0.2749	0.0982	0.5579	0.083*	0.5
C6	0.1614 (4)	−0.0070 (14)	0.5256 (6)	0.0853 (9)	0.5
H6A	0.1509	0.0549	0.4224	0.111*	0.5
H6B	0.1423	−0.1118	0.5038	0.111*	0.5
C7	0.1167 (2)	0.0611 (5)	0.6811 (6)	0.0819 (19)	0.5
H7	0.1369	0.1641	0.7140	0.098*	0.5
C8	0.0335 (2)	0.0232 (6)	0.7568 (9)	0.115 (2)	0.5
H8A	0.0060	0.1021	0.8258	0.149*	0.5
H8B	−0.0031	−0.0430	0.6897	0.149*	0.5
C9	0.37448 (16)	−0.0812 (3)	0.7500	0.0418 (6)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0584 (4)	0.0468 (3)	0.0486 (4)	0.000	0.000	0.0004 (3)

OW	0.0479 (13)	0.0488 (12)	0.0906 (17)	0.0055 (10)	0.000	0.000
O1	0.0438 (11)	0.0462 (11)	0.0842 (16)	−0.0067 (9)	0.000	0.000
O2	0.0428 (10)	0.0413 (11)	0.0967 (18)	0.0057 (8)	0.000	0.000
C4	0.0361 (13)	0.0468 (15)	0.0517 (17)	0.0021 (12)	0.000	0.000
C9	0.0377 (13)	0.0462 (15)	0.0416 (15)	−0.0013 (13)	0.000	0.000
C1	0.037 (2)	0.109 (4)	0.081 (4)	0.003 (3)	0.003 (2)	0.010 (4)
C2	0.0528 (13)	0.139 (3)	0.0644 (17)	0.0065 (17)	0.0150 (13)	−0.0114 (17)
C3	0.0470 (11)	0.096 (5)	0.0494 (17)	0.0065 (15)	−0.0001 (11)	−0.003 (3)
C5	0.0470 (11)	0.096 (5)	0.0494 (17)	0.0065 (15)	0.0001 (11)	0.003 (3)
C6	0.0528 (13)	0.139 (3)	0.0644 (17)	0.0065 (17)	−0.0150 (13)	0.0114 (17)
C7	0.043 (2)	0.111 (4)	0.092 (5)	0.018 (3)	−0.006 (2)	0.026 (4)
C8	0.046 (2)	0.169 (5)	0.128 (5)	0.020 (3)	0.042 (6)	0.002 (14)

Geometric parameters (Å, º)

K1—O1	2.719 (3)	C2—H2A	0.9700
K1—O1^i	2.719 (3)	C2—H2B	0.9700
K1—OW	2.779 (3)	C3—C4	1.538 (3)
K1—OW^i	2.779 (3)	C3—H3A	0.9700
K1—O2^{ii}	2.879 (3)	C3—H3B	0.9700
K1—O2^{iii}	2.879 (3)	C4—C9	1.528 (4)
K1—K1^{iv}	3.837 (5)	C4—C5	1.538 (4)
K1—HWA	2.85 (2)	C4—H4	0.9800
OW—K1^v	2.779 (3)	C5—C6	1.543 (3)
OW—HWA	0.822 (10)	C5—H5A	0.9700
OW—HWB	0.818 (10)	C5—H5B	0.9700
O1—C9	1.264 (3)	C6—C7	1.513 (4)
O2—C9	1.238 (3)	C6—H6A	0.9700
C1—C7	1.463 (6)	C6—H6B	0.9700
C1—C8	1.500 (4)	C7—C8	1.500 (4)
C1—C2	1.513 (4)	C7—H7	0.9800
C1—H1	0.9800	C8—H8A	0.9700
C2—C3	1.543 (3)	C8—H8B	0.9700
O1—K1—O1^i	148.36 (9)	C4—C3—H3A	107.8
O1—K1—OW	84.29 (10)	C2—C3—H3A	107.8
O1^i—K1—OW	88.63 (10)	C4—C3—H3B	107.8
O1—K1—OW^i	88.63 (10)	C2—C3—H3B	107.8
O1^i—K1—OW^i	84.29 (10)	H3A—C3—H3B	107.2
OW—K1—OW^i	153.85 (9)	C9—C4—C5	107.00 (18)
O1—K1—O2^{ii}	78.92 (8)	C9—C4—C3	108.6 (2)
O1^i—K1—O2^{ii}	126.41 (7)	C5—C4—C3	118.0 (3)
OW—K1—O2^{ii}	67.99 (7)	C9—C4—H4	107.6
OW^i—K1—O2^{ii}	135.07 (7)	C5—C4—H4	107.6
O1—K1—O2^{iii}	126.41 (7)	C3—C4—H4	107.6
O1^i—K1—O2^{iii}	78.92 (8)	C4—C5—C6	117.2 (4)
OW—K1—O2^{iii}	135.07 (7)	C4—C5—H5A	108.0
OW^i—K1—O2^{iii}	67.99 (7)	C6—C5—H5A	108.0

O2ⁱⁱ—K1—O2ⁱⁱⁱ	85.18 (10)	C4—C5—H5B	108.0
K1—OW—K1ᵛ	87.32 (11)	C6—C5—H5B	108.0
K1—OW—HWA	86.3 (18)	H5A—C5—H5B	107.2
K1ᵛ—OW—HWA	86.3 (18)	C7—C6—C5	107.1 (3)
K1—OW—HWB	134.1 (7)	C7—C6—H6A	110.3
K1ᵛ—OW—HWB	134.1 (7)	C5—C6—H6A	110.3
HWA—OW—HWB	111 (4)	C7—C6—H6B	110.3
C9—O1—K1	134.46 (6)	C5—C6—H6B	110.3
K1—O1—K1ᵛ	89.76 (11)	H6A—C6—H6B	108.5
C9—O2—K1ᵛⁱ	115.16 (11)	C1—C7—C8	60.80 (14)
K1ᵛⁱ—O2—K1ⁱⁱⁱ	83.57 (10)	C1—C7—C6	112.8 (5)
C7—C1—C8	60.82 (14)	C8—C7—C6	130.4 (4)
C7—C1—C2	112.9 (10)	C1—C7—H7	113.4
C8—C1—C2	130.4 (4)	C8—C7—H7	113.4
C7—C1—H1	113.3	C6—C7—H7	113.4
C8—C1—H1	113.3	C1—C8—C7	58.4 (3)
C2—C1—H1	113.3	C1—C8—H8A	117.9
C1—C2—C3	107.1 (3)	C7—C8—H8A	117.9
C1—C2—H2A	110.3	C1—C8—H8B	117.9
C3—C2—H2A	110.3	C7—C8—H8B	117.9
C1—C2—H2B	110.3	H8A—C8—H8B	115.1
C3—C2—H2B	110.3	O2—C9—O1	123.1 (2)
H2A—C2—H2B	108.5	O2—C9—C4	120.0 (2)
C4—C3—C2	117.8 (6)	O1—C9—C4	117.0 (2)
C1—C2—C3—C4	−28.1 (12)	C3—C2—C1—C7	−53.6 (9)
C7—C6—C5—C4	46.4 (12)	C2—C1—C7—C6	110.5 (5)
C2—C3—C4—C5	82.2 (8)	C2—C1—C7—C8	−124.8 (3)
C6—C5—C4—C3	−66.4 (8)	C6—C7—C1—C8	−124.8 (3)
C5—C6—C7—C1	−75.1 (8)		

Symmetry codes: (i) x, $−y+1/2$, $−z+1$; (ii) $−x+1$, $y+1/2$, z; (iii) $−x+1$, $−y$, $−z+1$; (iv) x, y, $−z+1/2$; (v) x, y, $−z+3/2$; (vi) $−x+1$, $−y$, $z+1/2$.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
OW—HWA···O1ⁱⁱ	0.82 (1)	1.88 (1)	2.701 (3)	180 (4)
OW—HWB···O2ᵛⁱⁱ	0.82 (1)	2.08 (3)	2.757 (4)	140 (3)

Symmetry codes: (ii) $−x+1$, $y+1/2$, z; (vii) x, $y+1$, z.

cis-**Bicyclo[5.1.0]octan-4-yl 4-bromobenzenesulfonate (II)**

Crystal data

$C_{14}H_{17}BrO_3S$	$V = 1461.2$ (3) Å³
$M_r = 345.24$	$Z = 4$
Monoclinic, $P2_1/c$	$F(000) = 704$
$a = 12.829$ (1) Å	$D_x = 1.569$ Mg m⁻³
$b = 9.759$ (1) Å	$D_m = 1.566$ Mg m⁻³
$c = 11.730$ (2) Å	D_m measured by density gradient column made
$β = 95.74$ (1)°	from potassium tartrate and iodide solutions

Cu *Kα* radiation, $\lambda = 1.5418$ Å
Cell parameters from 16 reflections
$\theta = 30.0°$
$\mu = 5.19$ mm^{-1}

$T = 297$ K
Block, colourless
$0.29 \times 0.24 \times 0.18$ mm

Data collection

Picker four-circle
   diffractometer
Radiation source: sealed X-ray tube
Oriented graphite 200 reflection
   monochromator
$\theta/2\theta$ scans
Absorption correction: gaussian
   Busing & Levy (1957)
$T_{min} = 0.267$, $T_{max} = 0.456$
2447 measured reflections

2381 independent reflections
2154 reflections with $I > 2\sigma(I)$
$R_{int} = 0.02$
$\theta_{max} = 63.4°$, $\theta_{min} = 3.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = -13 \rightarrow 13$
3 standard reflections every 100 reflections
   intensity decay: 2.4(8)

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.091$
$S = 1.08$
2381 reflections
173 parameters
0 restraints
Primary atom site location: heavy-atom method
Secondary atom site location: real-space vector
   search

Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 0.430P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Extinction correction: SHELXL2014
   (Sheldrick, 2015),
   Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.0062 (4)

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*	$U_{iso}*/U_{eq}$
Br	1.00989 (3)	0.32885 (3)	−0.39343 (3)	0.06640 (18)
S	0.74088 (5)	0.62673 (6)	−0.03759 (5)	0.04479 (19)
O1	0.69615 (16)	0.50385 (19)	0.02540 (14)	0.0595 (5)
O2	0.81339 (16)	0.70034 (19)	0.03968 (16)	0.0591 (5)
O3	0.65795 (18)	0.7021 (2)	−0.09750 (19)	0.0727 (6)
C1	0.5504 (3)	0.3765 (3)	0.3453 (3)	0.0671 (8)
H1	0.5006	0.3017	0.3269	0.081*
C2	0.5300 (2)	0.5028 (3)	0.2761 (2)	0.0524 (6)
H2A	0.5671	0.5788	0.3149	0.068*
H2B	0.4557	0.5234	0.2708	0.068*
C3	0.5639 (2)	0.4901 (3)	0.1548 (2)	0.0503 (6)
H3A	0.5464	0.3991	0.1256	0.065*

H3B	0.5248	0.5557	0.1052	0.065*
C4	0.6796 (2)	0.5145 (3)	0.15002 (19)	0.0463 (6)
H4	0.6967	0.6078	0.1767	0.056*
C5	0.7557 (2)	0.4164 (4)	0.2114 (2)	0.0646 (8)
H5A	0.8262	0.4406	0.1958	0.084*
H5B	0.7412	0.3246	0.1822	0.084*
C6	0.7495 (3)	0.4170 (4)	0.3420 (3)	0.0730 (9)
H6A	0.8149	0.3823	0.3797	0.095*
H6B	0.7413	0.5107	0.3671	0.095*
C7	0.6607 (3)	0.3324 (3)	0.3782 (3)	0.0782 (10)
H7	0.6722	0.2331	0.3777	0.094*
C8	0.5957 (4)	0.3823 (4)	0.4680 (3)	0.0919 (12)
H8A	0.6119	0.4718	0.5012	0.120*
H8B	0.5715	0.3154	0.5205	0.120*
C11	0.80882 (18)	0.5379 (2)	−0.13726 (19)	0.0399 (5)
C12	0.7890 (2)	0.5658 (3)	−0.2526 (2)	0.0506 (6)
H12	0.7356	0.6259	−0.2787	0.061*
C13	0.8491 (2)	0.5039 (3)	−0.3287 (2)	0.0544 (7)
H13	0.8372	0.5233	−0.4066	0.065*
C14	0.92621 (19)	0.4138 (3)	−0.2898 (2)	0.0452 (5)
C15	0.9459 (2)	0.3837 (3)	−0.1741 (2)	0.0540 (6)
H15	0.9985	0.3223	−0.1485	0.065*
C16	0.8865 (2)	0.4463 (3)	−0.0981 (2)	0.0504 (6)
H16	0.8984	0.4270	−0.0202	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0708 (3)	0.0710 (3)	0.0602 (2)	0.00970 (14)	0.02049 (16)	−0.01377 (14)
S	0.0477 (3)	0.0424 (3)	0.0456 (3)	−0.0021 (2)	0.0114 (3)	−0.0016 (2)
O1	0.0852 (14)	0.0547 (11)	0.0426 (9)	−0.0235 (10)	0.0260 (9)	−0.0096 (8)
O2	0.0678 (12)	0.0560 (11)	0.0553 (11)	−0.0186 (9)	0.0149 (9)	−0.0152 (9)
O3	0.0680 (13)	0.0787 (14)	0.0725 (13)	0.0296 (11)	0.0124 (11)	0.0048 (11)
C1	0.087 (2)	0.0559 (16)	0.0618 (17)	−0.0115 (16)	0.0251 (16)	0.0041 (14)
C2	0.0514 (14)	0.0613 (16)	0.0462 (13)	−0.0001 (12)	0.0133 (11)	−0.0045 (11)
C3	0.0543 (15)	0.0546 (15)	0.0423 (12)	−0.0010 (11)	0.0065 (11)	−0.0022 (11)
C4	0.0563 (14)	0.0484 (13)	0.0359 (11)	−0.0064 (11)	0.0133 (10)	−0.0054 (10)
C5	0.0561 (16)	0.079 (2)	0.0596 (16)	0.0130 (15)	0.0111 (13)	−0.0017 (15)
C6	0.0702 (19)	0.090 (2)	0.0566 (17)	0.0255 (18)	−0.0044 (14)	0.0041 (16)
C7	0.110 (3)	0.064 (2)	0.0631 (19)	0.0213 (18)	0.0215 (19)	0.0184 (14)
C8	0.133 (3)	0.091 (3)	0.0566 (18)	0.016 (2)	0.032 (2)	0.0242 (18)
C11	0.0412 (12)	0.0409 (12)	0.0380 (11)	−0.0032 (9)	0.0055 (9)	0.0019 (9)
C12	0.0560 (14)	0.0528 (14)	0.0424 (12)	0.0110 (12)	0.0018 (11)	0.0061 (11)
C13	0.0668 (17)	0.0610 (16)	0.0354 (12)	0.0088 (13)	0.0048 (12)	0.0040 (11)
C14	0.0456 (13)	0.0468 (13)	0.0440 (12)	−0.0005 (10)	0.0074 (10)	−0.0032 (10)
C15	0.0520 (14)	0.0601 (16)	0.0493 (14)	0.0162 (12)	0.0022 (11)	0.0036 (12)
C16	0.0553 (15)	0.0605 (15)	0.0352 (11)	0.0100 (12)	0.0040 (10)	0.0078 (11)

Geometric parameters (Å, º)

Br—C14	1.892 (2)	C5—C6	1.542 (4)
Br—O2[i]	3.2301 (19)	C5—H5A	0.9700
S—O3	1.421 (2)	C5—H5B	0.9700
S—O2	1.426 (2)	C6—C7	1.502 (5)
S—O1	1.5486 (18)	C6—H6A	0.9700
S—C11	1.755 (2)	C6—H6B	0.9700
O1—C4	1.502 (3)	C7—C8	1.489 (5)
O2—Br[ii]	3.2301 (19)	C7—H7	0.9800
C1—C2	1.485 (4)	C8—H8A	0.9700
C1—C8	1.499 (5)	C8—H8B	0.9700
C1—C7	1.493 (5)	C11—C12	1.379 (3)
C1—H1	0.9800	C11—C16	1.382 (3)
C2—C3	1.534 (3)	C12—C13	1.376 (4)
C2—H2A	0.9700	C12—H12	0.9300
C2—H2B	0.9700	C13—C14	1.368 (4)
C3—C4	1.510 (4)	C13—H13	0.9300
C3—H3A	0.9700	C14—C15	1.387 (4)
C3—H3B	0.9700	C15—C16	1.374 (4)
C4—C5	1.500 (4)	C15—H15	0.9300
C4—H4	0.9800	C16—H16	0.9300
C14—Br—O2[i]	170.06 (8)	H5A—C5—H5B	107.9
O3—S—O2	117.52 (14)	C7—C6—C5	113.3 (3)
O3—S—O1	110.01 (14)	C7—C6—H6A	108.9
O2—S—O1	109.64 (11)	C5—C6—H6A	108.9
O3—S—C11	108.87 (12)	C7—C6—H6B	108.9
O2—S—C11	109.64 (11)	C5—C6—H6B	108.9
O1—S—C11	99.66 (10)	H6A—C6—H6B	107.7
C4—O1—S	120.40 (15)	C8—C7—C1	60.3 (2)
S—O2—Br[ii]	107.81 (9)	C8—C7—C6	120.9 (3)
C2—C1—C8	121.6 (3)	C1—C7—C6	119.6 (3)
C2—C1—C7	119.5 (3)	C8—C7—H7	115.0
C8—C1—C7	59.7 (2)	C1—C7—H7	115.0
C2—C1—H1	115.0	C6—C7—H7	115.0
C8—C1—H1	115.0	C7—C8—C1	60.0 (2)
C7—C1—H1	115.0	C7—C8—H8A	117.8
C1—C2—C3	112.9 (2)	C1—C8—H8A	117.8
C1—C2—H2A	109.0	C7—C8—H8B	117.8
C3—C2—H2A	109.0	C1—C8—H8B	117.8
C1—C2—H2B	109.0	H8A—C8—H8B	114.9
C3—C2—H2B	109.0	C12—C11—C16	120.7 (2)
H2A—C2—H2B	107.8	C12—C11—S	120.07 (19)
C4—C3—C2	113.1 (2)	C16—C11—S	119.14 (17)
C4—C3—H3A	109.0	C13—C12—C11	119.3 (2)
C2—C3—H3A	109.0	C13—C12—H12	120.3
C4—C3—H3B	109.0	C11—C12—H12	120.3

C2—C3—H3B	109.0	C12—C13—C14	119.9 (2)
H3A—C3—H3B	107.8	C12—C13—H13	120.0
O1—C4—C5	105.9 (2)	C14—C13—H13	120.0
O1—C4—C3	105.10 (19)	C15—C14—C13	121.2 (2)
C5—C4—C3	118.5 (2)	C15—C14—Br	118.45 (19)
O1—C4—H4	109.0	C13—C14—Br	120.35 (18)
C5—C4—H4	109.0	C14—C15—C16	118.9 (2)
C3—C4—H4	109.0	C14—C15—H15	120.6
C4—C5—C6	112.2 (2)	C16—C15—H15	120.6
C4—C5—H5A	109.2	C11—C16—C15	120.0 (2)
C6—C5—H5A	109.2	C11—C16—H16	120.0
C4—C5—H5B	109.2	C15—C16—H16	120.0
C6—C5—H5B	109.2		
C1—C2—C3—C4	−81.7 (3)	C5—C6—C7—C1	−67.2 (4)
C7—C6—C5—C4	80.7 (4)	C2—C1—C7—C6	0.6 (5)
C2—C3—C4—C5	64.4 (3)	C2—C1—C7—C8	111.6 (3)
C6—C5—C4—C3	−63.4 (4)	C6—C7—C1—C8	−110.9 (4)
C3—C2—C1—C7	66.1 (4)		

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