Conformation and hydrogen bonding for the bicyclic compound 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide

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The initial goal of this work was to verify the geometry of the product of a photochemical reaction, *viz.* the title compound, $C_8H_{10}O_6S$, (II). Our crystallographic study firmly establishes the *cis–anti–cis* nature of the substituents on the cyclobutane ring. The geometry is also designated as *exo*, where *exo* signifies that the five-membered ring is on the opposite side of the central cyclobutane ring from the carboxylic acid substituents. The structure determination reveals two molecules, *A* and *B*, in the asymmetric unit that display substantially different conformations of the bicyclic core: the cyclobutane ring puckering angles are 22 and 3°, and the sulfolane ring conformations are twist (S-*exo*) and envelope (S-*endo*). Intrigued by this variation, we then compared the conformations of other molecules in the Cambridge Structural Database that have sulfolane rings fused to cyclobutane rings. In this class of compound, there are five examples of saturated cyclobutane rings, with ring puckering angles ranging from 3 to 35°. The sulfolane rings were more similar: four of the six molecules exhibit envelope conformations with S-*endo*, as in molecule *B* of (II). Despite the conformational differences, the hydrogen-bonding scheme for both molecules is similar: carboxyl –OH groups form hydrogen bonds with carboxyl and sulfone O atoms. Alternating *A* and *B* molecules joined by hydrogen bonds between sulfone O atoms and carboxyl –OH groups form parallel chains that extend in the *ac* plane. Other hydrogen bonds between the carboxyl groups link the chains along the *b* axis.

Comment

The photochemical addition of 3-sulfolene to maleic anhydride and its derivatives was first reported by Shaikhrazieva *et al.* (1971, 1972). A few years later the anhydride product, (I), known as the Bloomfield adduct, was patented by Monsanto as a chemical regulator of plant growth or development (Bloomfield, 1975). The various adducts formed by the addi-

tion of an alkene to 3-sulfolene have found considerable use in synthesis (Aitken *et al.*, 1999). The structure of (I) was determined at BP Research Centre, Sunbury-on-Thames, in 1982 by Smith (2003; see also Cadogan *et al.*, 1982) and the *exo* configuration was established by single-crystal X-ray diffraction; unfortunately, the crystallographic data were never published and are no longer available. Although the geometry of (I) could be predicted on mechanistic grounds, we deemed it worthwhile to determine it with certainty using X-ray crystallography. However, during the crystallization process, or at some other point, the anhydride ring was opened by water so that the structure actually determined was the title dicarboxylic acid, (II). The opening of the anhydride would not change the configuration of the substituents on the central cyclobutane ring.
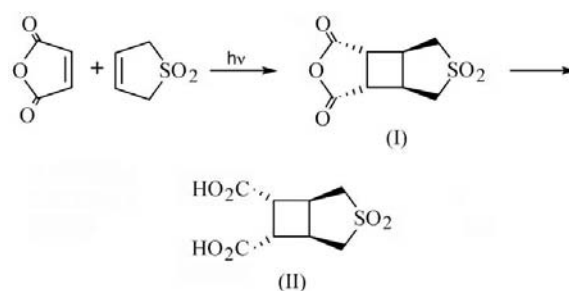

The X-ray crystal structure determination of (II) reveals two molecules, *A* and *B*, in the asymmetric unit. In both molecules, the geometry of the substituents on the central cyclobutane ring is *cis–anti–cis*. As shown in Fig. 1, each molecule has a chair-like structure, with the cyclobutane ring as the seat, the carboxyl groups the legs, the sulfolane ring the back and the sulfone group the headrest. The two molecules differ in the orientation of the sulfone group. In molecule *A* the headrest is tilted back, away from the cyclobutane ring, while in molecule *B* the headrest is tilted forward toward the cyclobutane ring, and the distance between sulfone atom O3′*B* and the plane of the cyclobutane ring is 2.96 Å. Other interatomic distances are given in Table 1.

In the *ac* plane, chains of alternating *A* and *B* molecules are linked headrest-to-legs by hydrogen bonds between the carboxyl –OH group and a sulfone O atom (Fig. 2). Along the
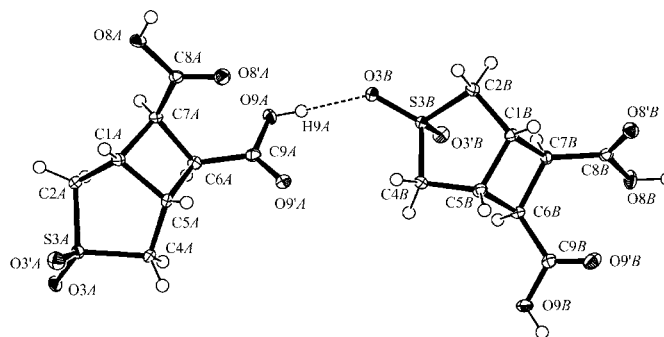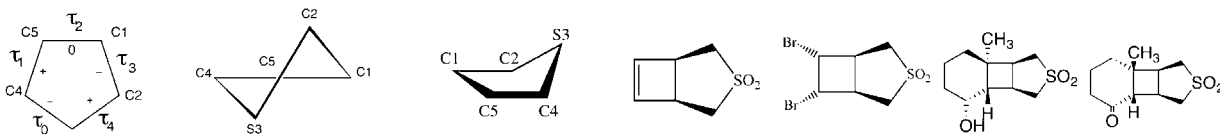

Figure 1
The two molecules in the asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The dashed line indicates a hydrogen bond.

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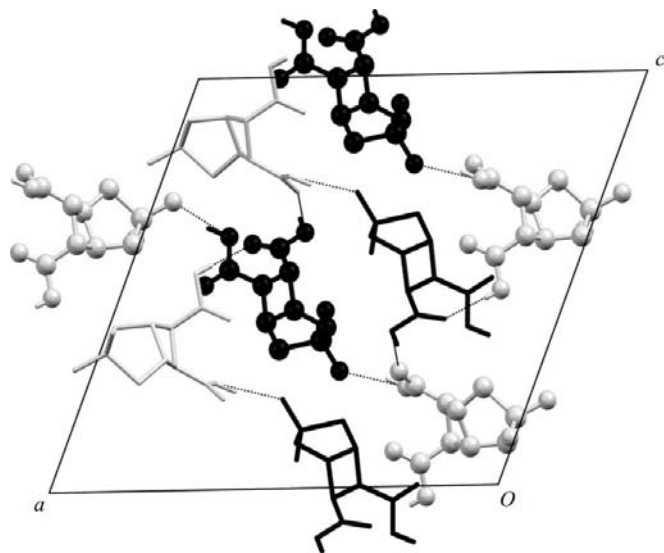
Figure 2
Packing diagram of (II) projected on the *ac* plane, showing parallel chains of alternating molecules *A* (grey) and *B* (black) extending along the *ac* plane. Two such chains lying close to the *ac* plane are shown as ball-and-stick structures. The chains are stabilized by dotted hydrogen bonds between sulfone atom O3*B* of molecule *B* and the –OH group (H9*A*) of the carboxylic acid substituent of molecule *A*. Three other hydrogen bonds between the carboxylic acid groups of molecules *A* and *B* extend along the *b* axis to form chains of *A* and *B* molecules, represented as wire frame structures. H atoms not involved in hydrogen bonds have been omitted for clarity.

b axis, hydrogen bonds between the carboxyl groups join molecule *A* to *B* and molecule *B* to *A*; details of the hydrogen-bonding scheme are given in Table 2.

The two molecules in the asymmetric unit of this structure exhibit two different low-energy conformations of the cyclobutane ring that are possible for this bicyclic compound.

Cyclobutane in the gas phase has a ring puckering angle of 28° (Egawa *et al.*, 1987). Presumably, puckering relieves torsional strain (Allen, 1984), but the solid-state structures of substituted cyclobutanes exhibit a wide range of puckering angles (Powell *et al.*, 1997; Allen *et al.*, 2005). For instance, in the structure of (II), molecule *A* is similar to an unsubstituted cyclobutane with a puckering angle of 22°, but the cyclobutane ring of molecule *B* is almost planar (puckering angle = 3°). Despite these differences in ring puckering, the average C—C distances and C—C—C angles in the two cyclobutane rings are the same within the uncertainty of measurement, and agree closely with those from a study (Allen, 1984) of puckered and planar cyclobutane derivatives in the Cambridge Structural Database.

Cyclopentane and substituted cyclopentane rings are non-planar, with two low-energy conformations, *viz.* twist (half-chair, symmetry C_2) and envelope (symmetry C_s) (Han & Kang, 1996; Riddell *et al.*, 1997). The various possible conformations are described by an imaginary pseudorotation process in which each atom in the ring in turn is displaced out of the plane, becoming the tip of the flap of the envelope. Envelope and twist conformations alternate every 18°. Traversing the complete pseudorotation cycle of 360° returns the ring to its original conformation. In actual cyclopentane structures, conformations intermediate between pure envelope and pure twist are observed. The calculated phase angle of pseudorotation (Altona & Sundaralingam, 1972) is useful to describe these intermediate conformations. For the sulfolane ring of molecule *A*, the pseudorotation angle is 246°, closest to pure twist at 252°, with the S atom *exo* (away from the cyclobutane ring) and C2 *endo*. In contrast, molecule *B* exhibits an envelope conformation (pseudorotation angle = 86°, closest to envelope at 90°), with the S atom at the tip of the flap, *endo* with respect to the cyclobutane ring.

	(II) Molecule A	(II) Molecule A, °	(II) Molecule B	(II) Molecule B, °	DOJPAT	DEKXEW	DIGNOW	DIGNIQ
τ_2	C4-C5-C1-C2	-19.1	C4-C5-C1-C2	2.8	-1.2	4.2	23.2	-5.43
τ_3	C5-C1-C2-S3	40.5	C5-C1-C2-S3	-26.2	-22.2	-22.5	3.01	-15.58
τ_4	C1-C2-S3-C4	-44.15	C1-C2-S3-C4	35.56	32.7	28.8	-23.2	26.69
τ_0	C2-S3-C4-C5	32.81	C2-S3-C4-C5	-33.9	-33.4	-26.6	36.94	-29.31
τ_1	S3-C4-C5-C1	-11.9	S3-C4-C5-C1	21.8	24.2	16.2	-37.89	23.77
P		246		86	92	82	305	100
Cyclopentane		Twist		Envelope	Envelope	Envelope	Envelope	Twist
conformation		S *exo*		S *endo*	S *endo*	S *endo*	C *endo*	S *endo*
Cyclobutane		22		3	0	5	35	13
pucker angle								

Figure 3
Table of torsion angles, phase angles of pseudorotation (*P*) and cyclobutane puckering angles in (II) and similar compounds from the Cambridge Structural Database. From left to right, the structural representations illustrate the nomenclature of the torsion angles in the sulfolane ring, with the signs of the torsion angles for the pure envelope conformation; the twist conformation for molecule *A* of (II); the envelope conformation for molecule *B* of (II); the chemical structures of similar compounds with data for each compound given in the column below. See Altona & Sundaralingam (1972) and Allen *et al.* (2005) for definitions and equations. CSD refcodes: DOJPAT = Cadogan *et al.* (1986); DEKXEW = Cadogan *et al.* (1985); DIGNOW and DIGNIQ = Williams *et al.* (1985).

Because of the two very different conformations exhibited in this structure, it is interesting to compare the conformations of other bicyclic and tricyclic compounds containing fused sulfolane and cyclobutane rings in the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002). These comparisons are shown in Fig. 3. The first diagram defines the torsion angles and shows that τ_2 is zero for the pure envelope conformation. The succeeding diagrams show the twist conformation for molecule A, the envelope conformation for molecule B, and the structural diagrams of the comparison molecules. Among the five molecules with saturated cyclobutane rings, the puckering angle varies from 3 to 35°, with molecule A of (II) and DIGNOW (Williams *et al.*, 1985) having the largest angle of puckering. DIGNOW and DIGNIQ (Williams *et al.*, 1985) are tricyclic compounds with a cyclohexane ring fused to the cyclobutane ring; in DIGNIQ the cyclohexane ring is *cis* to the cyclobutane ring, while in DIGNOW it is *trans*. The constraints imposed by the cyclohexane ring in these two structures may explain the moderate puckering of the cyclobutane ring in DIGNIQ and the large puckering in DIGNOW. No such constraints apply for molecule A, yet its puckering angle is relatively high.

Among the six sulfolane rings fused to cyclobutane, the preferred conformation is the envelope, with the S atom at the tip of the flap and *endo* to the cyclobutane ring, as in molecule B, but tricyclic DIGNOW has the envelope conformation with C4 *endo*. There are only two examples of the twist conformation, both with the S atom and adjacent C atom out of the plane, namely tricyclic DIGNIQ and molecule A of (II). Molecule A is unusual in several respects, having a relatively high puckering of the cyclobutane ring compared with the other bicyclic compounds, and is the only molecule in this bicyclic group with a twist conformation. The two molecules in (II) thus demonstrate the wide range of conformational variability possible in this bicyclic compound.

Experimental

The anhydride precursor, (I), to the title compound, (II), was synthesized by the photochemical [2+2]-cycloaddition of maleic anhydride and 3-sulfolene in acetone at room temperature following the directions of Bloomfield (1975). The initial product, (I), was hydrolyzed to (II), probably during crystallization. Colourless plates of (II) suitable for X-ray crystallographic determination were formed in a solution in acetone.

Crystal data

$C_8H_{10}O_6S$	$V = 1803.4\,(4)$ Å^3
$M_r = 234.22$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 18.497\,(3)$ Å	$\mu = 0.37$ mm^{-1}
$b = 6.1203\,(8)$ Å	$T = 103\,(2)$ K
$c = 17.188\,(2)$ Å	$0.36 \times 0.11 \times 0.05$ mm
$\beta = 112.051\,(2)°$	

Data collection

Bruker SMART area-detector diffractometer	13348 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	4458 independent reflections
$T_{min} = 0.877$, $T_{max} = 0.982$	3212 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.128$	
$S = 1.05$	
4458 reflections	$\Delta\rho_{max} = 0.71$ e Å^{-3}
283 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected bond lengths (Å).

S3A—O3′A	1.440 (2)	S3B—O3′B	1.438 (2)
S3A—O3A	1.456 (2)	S3B—O3B	1.446 (2)
S3A—C2A	1.774 (3)	S3B—C2B	1.771 (3)
S3A—C4A	1.781 (3)	S3B—C4B	1.779 (3)
C1A—C2A	1.523 (4)	C5B—C4B	1.524 (4)
C1A—C5A	1.570 (4)	C5B—C1B	1.565 (4)
C5A—C4A	1.536 (4)	C1B—C2B	1.529 (4)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O8A—H8$A\cdots$O9′B^i	0.69 (4)	1.99 (4)	2.686 (3)	178 (5)
O9A—H9$A\cdots$O3B	0.84 (4)	2.02 (4)	2.834 (3)	163 (3)
O9B—H9$B\cdots$O9′A^{ii}	0.80 (4)	1.83 (4)	2.618 (3)	166 (4)
O8B—H8$B\cdots$O3A^{iii}	0.94 (4)	1.78 (4)	2.700 (3)	165 (3)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+3, -z+1$; (iii) $x+1, -y+\frac{5}{2}, z+\frac{1}{2}$.

In order to compare the structure of (II) with those of other molecules in the Cambridge Structural Database, *PREQUEST* and *ACTIVATE* (Cambridge Crystallographic Data Centre, 1994) were used to format the CIF file for the CSD. The CSD (Version 5.29; Allen, 2002) was then searched using *CONQUEST* (Bruno *et al.*, 2002) for other fused sulfolane–cyclobutane structures. Torsion angles in the sulfolane ring and the dihedral angle in the cyclobutane ring were calculated using *VISTA* (Cambridge Crystallographic Data Centre, 1994). The pseudorotation angle for the sulfolane rings was calculated and the conformation assigned using the definitions of Altona & Sundaralingam (1972). The cyclobutane puckering angle was calculated using the definition of Allen *et al.* (2005). Because they participate in hydrogen bonding, the positions of atoms H8A, H9A, H8B and H9B were refined, with $U_{iso}(H) = 1.2U_{eq}(O)$. Idealized positions for other H atoms were calculated at 0.93 Å from bonded C atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*, *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

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