O1*A*—S1*A*—O2*A*	121.0 (2)	S1*A*—C1*A*—C2*A*	120.6 (4)
O1*A*—S1*A*—N1*A*	107.3 (2)	S1*A*—C1*A*—C6*A*	119.3 (4)
O1*A*—S1*A*—C1*A*	107.2 (2)	C2*A*—C1*A*—C6*A*	120.1 (5)
O2*A*—S1*A*—N1*A*	104.5 (2)	C1*A*—C2*A*—C3*A*	118.6 (5)
O2*A*—S1*A*—C1*A*	108.9 (2)	C1—C2—C3	119.7 (5)
N1*A*—S1*A*—C1*A*	107.1 (2)	C2—C3—C4	122.0 (5)
O1—S1—O2	120.3 (2)	C2*A*—C3*A*—C4*A*	122.9 (6)
O1—S1—N1	105.7 (2)	C3*A*—C4*A*—C5*A*	118.0 (5)
O1—S1—C1	108.0 (2)	C3*A*—C4*A*—C7*A*	121.8 (6)
O2—S1—N1	103.0 (2)	C5*A*—C4*A*—C7*A*	120.2 (6)
O2—S1—C1	110.8 (2)	C3—C4—C5	116.8 (5)
N1—S1—C1	108.3 (2)	C3—C4—C7	120.6 (5)
S1—N1—N1*A*	112.8 (3)	C5—C4—C7	122.6 (5)
S1*A*—N1*A*—N1	114.4 (3)	C4—C5—C6	122.8 (5)
S1—C1—C2	119.5 (4)	C4*A*—C5*A*—C6*A*	121.0 (6)
S1—C1—C6	120.0 (4)	C1*A*—C6*A*—C5*A*	119.3 (6)
C2—C1—C6	120.4 (4)	C1—C6—C5	118.3 (5)

Table 3. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1*A*^{i}	0.95	2.03 (1)	2.921 (5)	155 (1)
N1*A*—H1NA···O1^{i}	0.95	1.95 (1)	2.847 (5)	156 (1)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

In (1), the positional parameters of the H atoms were refined [C—H range: 0.91 (2)–1.02 (2) Å]. In (2), all H atoms were placed in calculated positions. In light of the near twofold symmetry of the molecules in (2), a precautionary check for higher symmetry was conducted using the program *MISSYM* (Le Page, 1987); none was found.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1031). Services for accessing these data are described at the back of the journal.

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Cyclopentanone Tosylhydrazone and Cyclohexanone Tosylhydrazone

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Abstract

The crystal structures of 2-cyclopentylidene-1-(*p*-toluenesulfono)hydrazide [cyclopentanone tosylhydrazone, $C_{12}H_{16}N_2O_2S$, (1)] and 2-cyclohexylidene-1-(*p*-toluenesulfono)hydrazide [cyclohexanone tosylhydrazone, $C_{13}H_{18}N_2O_2S$, (2)] are described. In both structures, the conformation of the N—N—S—O linkage is *anti*, with torsion angles of −173.5 (1)° in (1) and 174.9 (1)° in (2), giving the molecules as a whole a folded appearance. In the cyclopentyl structure, the phenyl ring is twisted away from any eclipsing interaction with either S—O bond, but in the cyclohexyl structure, it is eclipsed with the S—O bond [torsion angle 1.4 (2)°]. In both structures, the packing arrangement features centrosymmetrically hydrogen-bonded pairs of molecules, with the *anti* O atom as the acceptor atom [N···O distance of 2.986 (2) Å in (1) and 2.969 (2) Å in (2)].

Comment

As part of our ongoing study of the interactions between proteins and sulfated carbohydrates, we have previously determined the crystal structures of several sugar derivatives prepared by the reaction of monosaccharides with phenylhydrazine or toluenesulfonhydrazide (Ojala & Gleason, 1996; Ojala, Ojala & Gleason, 1997). Depending on the monosaccharide, such a derivative can assume a cyclic form and exist as an *N*-glycoside or assume an acyclic form and exist as a hydrazone. In an effort to identify bands in the infrared spectra of these derivatives which would be readily diagnostic for a particular form, we have also prepared and examined the tosylhydrazones of non-carbohydrate compounds which must yield hydrazones rather than cyclic structures. Our aim is to be able use their infrared spectra for comparison purposes. In a previous report we have described the crystal structures of two polymorphs of one of these true hydrazones, acetone tosylhydrazone (Ojala, Ojala, Pennamon & Gleason, 1998). We describe here the crystal

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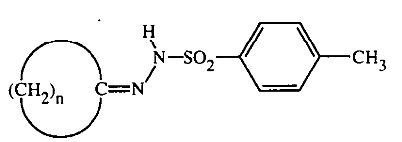
structures of two additional examples, cyclopentanone tosylhydrazone, (1) and cyclohexanone tosylhydrazone, (2).



(1) *n* = 4
(2) *n* = 5

The molecular conformations and atom-numbering schemes for (1) and (2) are shown in Figs. 1 and 2, respectively. Both compounds (1) and (2) assume an *anti* conformation across the N1—N2—S1—O2 linkage [−173.5 (1) and 174.9 (1)° in (1) and (2), respectively], giving molecules in both structures a folded appearance due to the resulting *gauche* relationship, across the S1—N2 bond, between the aryl ring and the *N*-substituted cycloalkyl group. Consistent with delocalization of the N2 lone electron pair into the sulfonyl group, the *anti* S1—O2 bond is significantly longer than the S1—O1 bond in both (1) and (2).

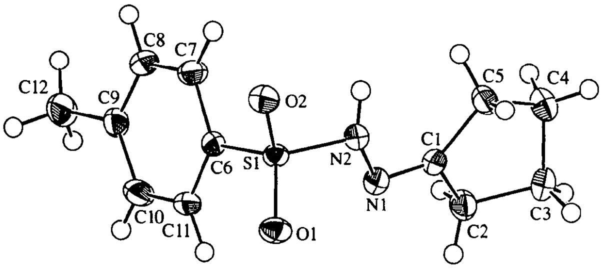


Fig. 1. *ORTEP*II (Johnson, 1976) view of (1) showing the atom numbering. For non-H atoms, 50% probability ellipsoids are shown.

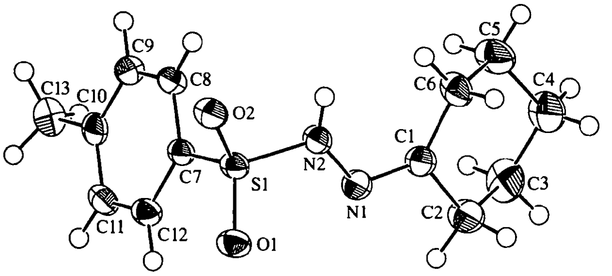


Fig. 2. *ORTEP*II (Johnson, 1976) view of (2) showing the atom numbering. For non-H atoms, 50% probability ellipsoids are shown.

In our description of the crystal structures of the acetone tosylhydrazone polymorphs, we noted that they are conformational polymorphs, differing from each other in the orientation of the phenyl ring with respect to the sulfonyl S—O bonds. In one of these two crystalline forms, the conformation of the molecule is such that an S—O bond is eclipsed by the phenyl ring; in the other, neither S—O bond is eclipsed. Conformational differences of this type are also found in the cyclopentyl and cyclohexyl tosylhydrazones described here. In (1), neither S—O bond is eclipsed by the phenyl ring, but in (2), one of the S—O bonds is eclipsed with respect to the phenyl ring [O1—S1—C7—C12 1.4 (2)°]. Workers interested in polymorphism may wish to consider whether an eclipsed version of (1) and a staggered version of (2) could be additional forms of these structures that are in theory obtainable but as yet remain unprepared.

The packing arrangements assumed by (1) and (2) are shown in Figs. 3 and 4, respectively. In each structure, molecules are joined pairwise *via* hydrogen bonds about crystallographic inversion centers, the *anti* O atom acting as the acceptor atom. The same centrosymmetric hydrogen-bonding arrangement, also with the *anti* O atom as acceptor, is found in the two polymorphs of acetone tosylhydrazone described previously.

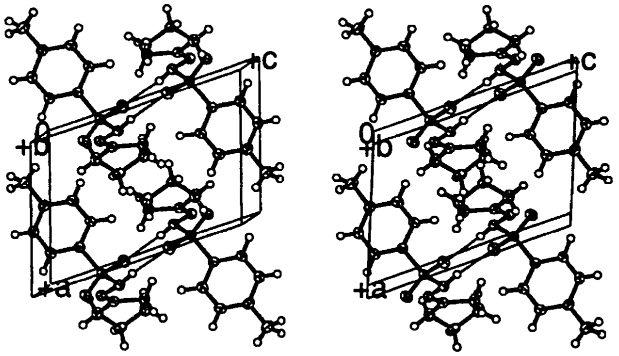


Fig. 3. Stereoview of the molecular packing in (1). Hydrogen bonds are shown as narrow lines.

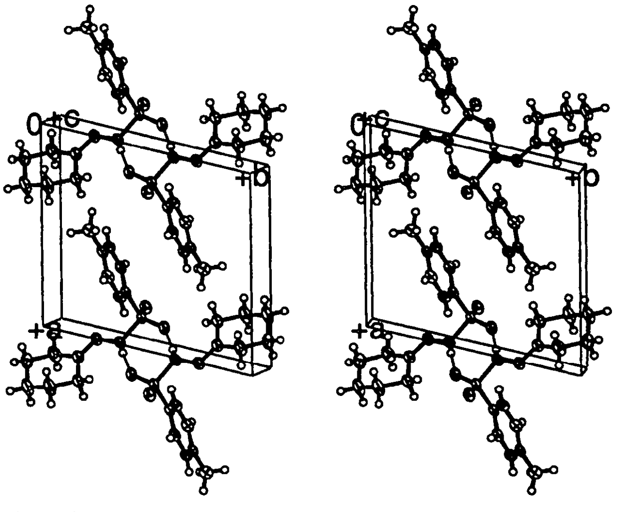


Fig. 4. Stereoview of the molecular packing in (2). Hydrogen bonds are shown as narrow lines.

Experimental

Compounds (1) and (2) were prepared using standard methods.

Compound (1)

Crystal data

$C_{12}H_{16}N_2O_2S$
$M_r = 252.33$
Triclinic
$P\bar{1}$
$a = 8.268\ (1)$ Å
$b = 8.483\ (1)$ Å
$c = 10.802\ (2)$ Å
$\alpha = 108.85\ (2)°$
$\beta = 101.33\ (2)°$
$\gamma = 111.43\ (1)°$
$V = 623.4\ (5)$ Å^3
$Z = 2$
$D_x = 1.344$ Mg m^{-3}
D_m not determined

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 41.0$–$50.0°$
$\mu = 2.202$ mm^{-1}
$T = 173$ K
Prism
0.36 × 0.16 × 0.12 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.667$, $T_{\max} = 0.768$
3683 measured reflections
2352 independent reflections

2225 reflections with $I > 3\sigma(I)$
$R_{\text{int}} = 0.035$
$\theta_{\max} = 69.94°$
$h = -10 \rightarrow 9;\ -7 \rightarrow 8$
$k = -10 \rightarrow 9;\ -7 \rightarrow 8$
$l = 0 \rightarrow 13;\ -10 \rightarrow -1$
3 standard reflections frequency: 60 min intensity decay: 5.11%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.058$
$S = 2.656$
2225 reflections
203 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.0005$

$\Delta\rho_{\max} = 0.75$ e Å^{-3}
$\Delta\rho_{\min} = -0.60$ e Å^{-3}
Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 0.3421×10^{-4}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °) for (1)*

S1—O1	1.429 (1)	C3—C4	1.525 (3)
S1—O2	1.446 (1)	C4—C5	1.538 (2)
S1—N2	1.643 (1)	C6—C7	1.395 (2)
S1—C6	1.755 (2)	C6—C11	1.387 (2)
N1—N2	1.406 (2)	C7—C8	1.383 (3)
N1—C1	1.277 (2)	C8—C9	1.391 (3)
C1—C2	1.506 (2)	C9—C10	1.398 (2)
C1—C5	1.511 (2)	C9—C12	1.507 (2)
C2—C3	1.530 (2)	C10—C11	1.386 (3)
O1—S1—O2	119.44 (7)	C3—C4—C5	104.7 (1)
O1—S1—N2	108.14 (7)	C1—C5—C4	104.1 (1)
O1—S1—C6	108.59 (8)	S1—C6—C7	118.6 (1)
O2—S1—N2	103.41 (7)	S1—C6—C11	120.3 (1)
O2—S1—C6	108.99 (7)	C7—C6—C11	121.1 (2)
N2—S1—C6	107.66 (7)	C6—C7—C8	118.9 (2)
N2—N1—C1	115.1 (1)	C7—C8—C9	121.3 (2)
S1—N2—N1	113.0 (1)	C8—C9—C10	118.6 (2)
N1—C1—C2	121.3 (2)	C8—C9—C12	120.0 (2)
N1—C1—C5	128.6 (2)	C10—C9—C12	121.4 (2)
C2—C1—C5	110.1 (1)	C9—C10—C11	121.2 (2)
C1—C2—C3	103.2 (1)	C6—C11—C10	118.9 (2)
C2—C3—C4	104.0 (1)		
S1—N2—N1—C1	170.9 (1)	N2—S1—C6—C7	−77.1 (1)
O1—S1—N2—N1	58.9 (1)	N2—S1—C6—C11	100.8 (1)
O1—S1—C6—C7	166.1 (1)	N2—N1—C1—C2	178.7 (1)
O1—S1—C6—C11	−16.1 (2)	N2—N1—C1—C5	1.9 (2)
O2—S1—N2—N1	−173.5 (1)	C1—C2—C3—C4	−34.4 (2)
O2—S1—C6—C7	34.4 (1)	C1—C5—C4—C3	−24.9 (2)
O2—S1—C6—C11	−147.7 (1)	C2—C1—C5—C4	3.4 (2)
N1—N2—S1—C6	−58.3 (1)	C2—C3—C4—C5	37.2 (2)
N1—C1—C2—C3	−158.1 (1)	C3—C2—C1—C5	19.2 (2)
N1—C1—C5—C4	−179.5 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O2$^{\text{i}}$	0.86 (2)	2.14 (3)	2.986 (2)	167 (3)

Symmetry code: (i) $-x, 1-y, 1-z$.

Compound (2)

Crystal data

$C_{13}H_{18}N_2O_2S$
$M_r = 266.36$
Triclinic
$P\bar{1}$
$a = 10.1893\ (8)$ Å
$b = 11.0454\ (8)$ Å
$c = 6.1106\ (5)$ Å
$\alpha = 99.258\ (6)°$
$\beta = 93.769\ (7)°$
$\gamma = 75.799\ (5)°$
$V = 657.8\ (2)$ Å^3
$Z = 2$
$D_x = 1.345$ Mg m^{-3}
D_m not determined

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 48.8$–$50.0°$
$\mu = 2.113$ mm^{-1}
$T = 173$ K
Plate
0.48 × 0.32 × 0.08 mm
Colorless

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.608$, $T_{\max} = 0.844$
4853 measured reflections
2428 independent reflections
2020 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.032$
$\theta_{\max} = 70.12°$
$h = 0 \rightarrow 12;\ -12 \rightarrow -1$
$k = -13 \rightarrow 13;\ -13 \rightarrow 12$
$l = -7 \rightarrow 7;\ -7 \rightarrow 7$
3 standard reflections every 150 reflections intensity decay: −2.60%

Refinement

Refinement on F
$R = 0.034$
$wR = 0.039$
$S = 2.194$
2020 reflections
218 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.0024$

$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 0.4335×10^{-5}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (2)*

S1—O1	1.431 (1)	C4—C5	1.515 (3)
S1—O2	1.441 (1)	C5—C6	1.524 (3)
S1—N2	1.626 (2)	C7—C8	1.394 (3)
S1—C7	1.760 (2)	C7—C12	1.387 (3)
N1—N2	1.390 (2)	C8—C9	1.378 (3)
N1—C1	1.288 (2)	C9—C10	1.388 (3)
C1—C2	1.501 (3)	C10—C11	1.394 (3)
C1—C6	1.491 (3)	C10—C13	1.499 (3)
C2—C3	1.522 (3)	C11—C12	1.384 (3)
C3—C4	1.513 (4)		
O1—S1—O2	119.49 (8)	C3—C4—C5	110.7 (2)
O1—S1—N2	109.66 (8)	C4—C5—C6	111.8 (2)
O1—S1—C7	107.60 (9)	C1—C6—C5	111.8 (2)
O2—S1—N2	103.63 (8)	S1—C7—C8	118.9 (2)
O2—S1—C7	108.54 (8)	S1—C7—C12	120.3 (1)
N2—S1—C7	107.35 (8)	C8—C7—C12	120.7 (2)
N2—N1—C1	117.5 (2)	C7—C8—C9	118.8 (2)
S1—N2—N1	116.2 (1)	C8—C9—C10	121.7 (2)
N1—C1—C2	115.9 (2)	C9—C10—C11	118.6 (2)
N1—C1—C6	127.6 (2)	C9—C10—C13	120.9 (2)
C2—C1—C6	116.3 (2)	C11—C10—C13	120.6 (2)
C1—C2—C3	112.9 (2)	C10—C11—C12	120.8 (2)
C2—C3—C4	111.1 (2)	C7—C12—C11	119.4 (2)
S1—N2—N1—C1	172.8 (1)	N2—S1—C7—C8	−62.7 (2)
O1—S1—N2—N1	46.3 (2)	N2—S1—C7—C12	119.4 (1)
O1—S1—C7—C8	179.4 (1)	N2—N1—C1—C2	171.7 (2)
O1—S1—C7—C12	1.4 (2)	N2—N1—C1—C6	−2.3 (3)
O2—S1—N2—N1	174.9 (1)	C1—C2—C3—C4	50.4 (3)
O2—S1—C7—C8	48.7 (2)	C1—C6—C5—C4	−51.6 (3)
O2—S1—C7—C12	−129.2 (1)	C2—C1—C6—C5	46.0 (3)
N1—N2—S1—C7	−70.3 (2)	C2—C3—C4—C5	−57.0 (3)
N1—C1—C2—C3	139.3 (2)	C3—C2—C1—C6	−46.0 (3)
N1—C1—C6—C5	−140.0 (2)	C3—C4—C5—C6	58.1 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O2^{i}	0.81 (2)	2.17 (2)	2.969 (2)	169 (2)

Symmetry code: (i) $-x, 1-y, -z$.

In both (1) and (2), only the H-atom positions were refined; in (1), N—H = 0.86 (2) and C—H = 0.88 (3)–1.03 (3) Å, while in (2), N—H = 0.81 (2) and C—H = 0.87 (2)–1.02 (2) Å].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989) for (1); *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (2). Cell refinement: *CAD*-4 *Software* for (1); *MSC/AFC Diffractometer Control Software* for (2). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

We thank the Minnesota Medical Foundation and the graduate school of the University of Minnesota for partial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1033). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 66–68

Methoxyamericanolide B†

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(*Received 22 November 1996; accepted 4 September 1997*)

Abstract

The title compound, $C_{16}H_{20}O_5$, was isolated from the gorgonian coral *P. americana* found in the Caribbean zone of the West Indies. The compound belongs to a well known family of sesquiterpenoid lactones. Its structure features a guaiane skeleton incorporating three types of oxygen functionalities. Thus, the five O atoms that are incorporated in the skeleton form two epoxy groups, a lactone moiety and an ether link. This study assigns the relative stereochemistry at the six chiral centers as 1*R*,2*R*,4*S*,5*S*,8*R*,10*S*.

Comment

Pseudopterogorgia americana is widespread in the Caribbean zone of the West Indies and contains a large number of pharmacologically active compounds (Rodríguez, 1995). As part of our continued investigation of the sea plume *P. americana* from Puerto Rico, we isolated and spectroscopically identified a new compound, methoxyamericanolide B, (I). In order to confirm the identity and to reveal the absolute stereochemistry of this compound, a single-crystal X-ray structure analysis was carried out.

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† Systematic name: 7-methoxy-4,9,13-trimethyl-6-oxa-1,13:10,11-diepoxytricyclo[8.3.0.0^{3,7}]tridec-3-en-5-one.

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