

2,2,4,4-Tetramethyl-1,5-diphenyl-6,7,8-trioxa-3-thiabicyclo[3.2.1]-octane

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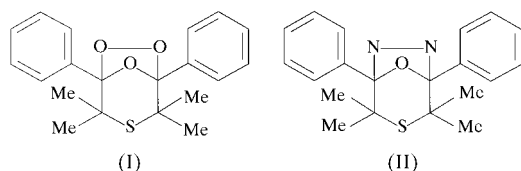
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The structure of the title ozonide, $C_{20}H_{22}O_3S$, produced without the use of ozone, has been defined at 123 (1) K. In the triclinic crystal, the molecule has symmetry close to C_s , and its ozonide and 1,4-oxathiane rings have envelope and chair conformations, respectively. The ozonide unit has an O—O bond length of 1.4721 (12) Å and a C—O—O—C torsion angle of -1.45 (12)°.

Comment

Conventionally, ozonides are prepared by the action of molecular ozone, O_3 , on alkenes (March, 1992). We have described the facile high-yield formation of a stable ozonide, (I), by air (or neat O_2) oxidation of 2,2,4,4-tetramethyl-1,5-diphenyl-8-oxa-3-thia-6,7-diazabicyclo[3.2.1]octane, (II), in benzene solution at room temperature (Cuthbertson *et al.*, 1975). The present communication gives the first structural details concerning this novel ozonide, (I), and reports the outcome of a literature survey of ozonides undertaken to establish any relationship between the O—O bond length and the endocyclic C—O—O—C torsion angle.



The molecule of (I) has symmetry close to C_s , with a non-crystallographic mirror plane passing through O3 and S1, and bisecting the ozonide O—O bond, as illustrated in Fig. 1. The symmetry may also be appreciated by consideration of the following pairs of corresponding torsion angles: O1—O2—C14—O3/O2—O1—C7—O3 of -20.8 (1)/ 23.0 (1)°, O3—C7—C8—S1/O3—C14—C11—S1 of -60.5 (1)/ 60.7 (1)° and O1—C7—C1—C2/O2—C14—C15—C16 of 36.3 (2)/ -33.5 (2)°.

Selected structural parameters, including other torsion angles, are given in Table 1. The close approach to C_s symmetry in (I) also extends to the bond lengths (Table 1) and, interestingly, the marked asymmetry often found for the C—O bonds involving the peroxy moiety of the ozonide (Tzou *et al.*, 1996) is not present in (I), since the O1—C7 and O2—C14 bond lengths [1.4509 (15) and 1.4517 (15) Å, respectively] do not differ significantly.

The ozonide ring has an envelope conformation, with O3 displaced by -0.513 (2) Å from the mean plane of C7, O1, O2 and C14, which are coplanar (r.m.s. deviation 0.007 Å). The six-membered 1,4-oxathiane ring has a chair conformation, with C7, C8, C11 and C14 coplanar (r.m.s. deviation 0.000 Å),

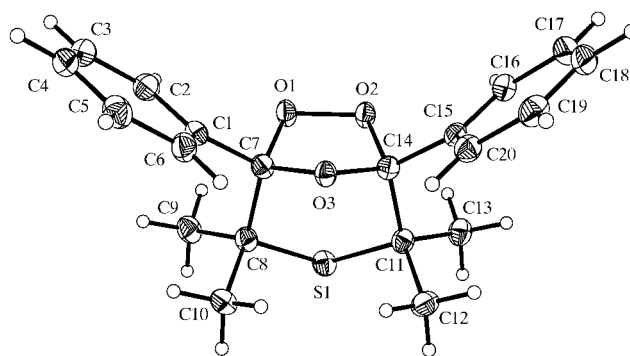


Figure 1

A molecular view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

and S1 and O3 displaced by -0.684 (2) and 0.807 (1) Å, respectively, from this mean plane. Comparison of the angle α subtended between the planes defined by C8, S1 and C11, and C7, C8, C11 and C14 [37.27 (5)°] with the corresponding α parameter for a system unconstrained by bridging, such as *trans*-2,3-dichloro-1,4-oxathiane (46.1° ; Desseyn *et al.*, 1972), indicates the presence of an inverse reflex effect (Jefford *et al.*, 1970). Thus 'pinching' brought about by the *syn*-axial placement of the O—O bridge in (I) results in a displacement of S1 towards the plane described by the four C atoms, with a corresponding decrease in the value of α . The corresponding value of α in (II), reflecting the presence of its two-atom hydrazo bridge, is 36.2° (Cuthbertson *et al.*, 1975).

Searching the Cambridge Structural Database (CSD; Allen & Kennard, 1993) for the five-membered ozone substructure [C7, O1, O2, C14 and O3 in (I)] identifies 47 crystallographically unique fragments. The O—O bond length in (I) of 1.4721 (12) Å is indistinguishable from the average value for these 47 ozonides of 1.473 (11) Å and may be compared with the value of 1.481 (10) Å for the corresponding bond in 3,4 α ,5,7,8,8 α -hexahydro-3,3-dimethyl-7 β ,8 $\alpha\beta$ -diphenyl-5 α ,7 α -epidioxypyranolo[3,4-*e*]-1,2,4-trioxane at 295 K (Bernardinelli *et al.*, 1987), the respective C—O—O—C torsion angles being -1.45 (12) and 7.4 (8)°. The majority of the O—O bond lengths lie in the range ~ 1.46 – 1.50 Å, with a wide range of C—O—O—C torsion angles spanning 0 to $\sim 50^\circ$.

Seeking to establish whether or not a correlation exists between the O—O bond length and the C—O—O—C torsion angle in the ozone ring, a scattergram of O—O distance *versus* C—O—O—C torsion angle was generated. No apparent general correlation between these two parameters was revealed, with 27 cases having a torsion angle in a narrow range of 0 to $\pm 10^\circ$ and with O—O bond lengths spanning ~ 1.445 – 1.497 Å. Interestingly, a relatively isolated group of ten cases with torsion angles in the range ± 40 – 50° displayed a narrower range of O—O bond lengths [~ 1.465 – 1.475 Å], possibly reflecting a reduced range of strain energy associated with relaxation of the endocyclic C—O—O—C torsion angle.

A packing diagram for (I) is shown in Fig. 2. There are no formal hydrogen bonds present in the structure, although the packing diagram reveals both a π – π ring-stacking interaction and a C—H $\cdots\pi$ edge-to-face interaction with a centrosymmetrically related molecule; contact distances are given in Table 2.

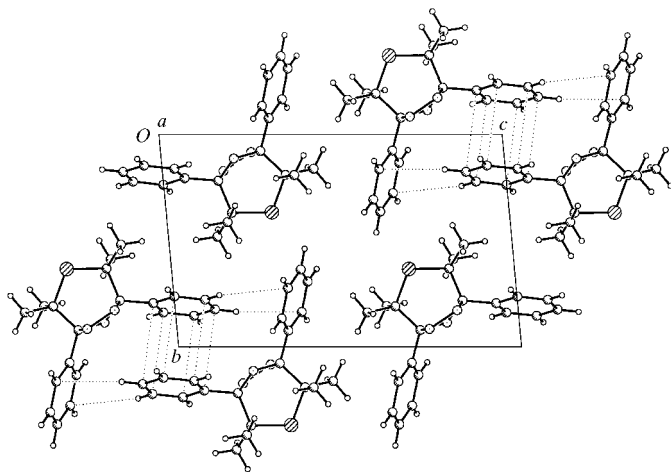


Figure 2
The molecular packing of (I) in the triclinic crystal, viewed along **a**.

Experimental

Compound (I) was prepared as described previously by Cuthbertson *et al.* (1975) and was recrystallized from ethanol, giving colourless needles [m.p. 455–458 K (decomposition)].

Crystal data

$C_{20}H_{22}O_3S$	$Z = 2$
$M_r = 342.44$	$D_x = 1.330$ Mg m $^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.0507$ (5) Å	Cell parameters from 5133 reflections
$b = 9.6570$ (9) Å	$\theta = 2.18$ – 29.07°
$c = 15.4541$ (14) Å	$\mu = 0.204$ mm $^{-1}$
$\alpha = 82.093$ (8) $^\circ$	$T = 123$ (1) K
$\beta = 78.738$ (6) $^\circ$	Prism, colourless
$\gamma = 75.898$ (5) $^\circ$	$0.40 \times 0.25 \times 0.20$ mm
$V = 855.08$ (13) Å 3	

Data collection

Bruker 1 K CCD area-detector diffractometer	$R_{int} = 0.015$
Narrow frame ω scans	$\theta_{max} = 26.37^\circ$
7324 measured reflections	$h = -7 \rightarrow 7$
3459 independent reflections	$k = -12 \rightarrow 12$
2844 reflections with $I > 2\sigma(I)$	$l = -18 \rightarrow 19$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
$wR(F^2) = 0.097$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.017$	$(\Delta/\sigma)_{max} < 0.001$
3459 reflections	$\Delta\rho_{max} = 0.31$ e Å $^{-3}$
221 parameters	$\Delta\rho_{min} = -0.26$ e Å $^{-3}$

Table 1

Selected geometric parameters (Å, $^\circ$).

S1—C11	1.8378 (14)	O3—C7	1.4202 (15)
S1—C8	1.8389 (14)	C1—C7	1.5139 (19)
O1—C7	1.4509 (15)	C7—C8	1.5513 (19)
O1—O2	1.4721 (12)	C11—C14	1.5511 (19)
O2—C14	1.4517 (15)	C14—C15	1.5181 (18)
O3—C14	1.4158 (15)		
C11—S1—C8	104.21 (6)	O1—C7—C8	110.89 (11)
C7—O1—O2	105.75 (8)	C7—C8—S1	108.56 (9)
C14—O2—O1	105.96 (8)	C14—C11—S1	108.36 (9)
C14—O3—C7	106.04 (9)	O3—C14—O2	104.25 (10)
O3—C7—O1	103.96 (10)	O3—C14—C11	110.85 (10)
O3—C7—C8	110.57 (10)	O2—C14—C11	110.08 (10)
C7—O1—O2—C14	−1.45 (12)	O1—O2—C14—O3	−20.78 (12)
O2—O1—C7—O3	23.04 (12)	S1—C11—C14—O3	60.68 (12)
C2—C1—C7—O1	36.27 (16)	O2—C14—C15—C16	−33.50 (16)
O3—C7—C8—S1	−60.49 (12)		

Table 2

Contact distances (Å).

C1 \cdots C4 i	3.813 (2)	H3A \cdots C19 i	3.22
C2 \cdots C5 i	3.830 (2)	H4A \cdots C16 i	2.97
C3 \cdots C6 i	3.829 (2)		

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

H atoms were placed geometrically, with C—H = 0.95 Å (0.98 Å for methyl H atoms), and refined with a riding model (including free rotation about C—C bonds for methyl groups), with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART* and *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1303). Services for accessing these data are described at the back of the journal.

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