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7,7-Dichloro-1,6-dimethyl-2-oxa-5-thiabicyclo[4.1.0]heptane 5,5-dioxide and 6-chloro-2,3-dihydro-7-methyl-5-methylene-2*H*,3*H*,5*H*-1,4-dithiepine 1,1,4,4-tetraoxide

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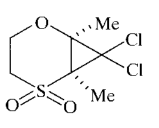
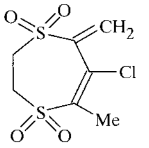
The structures of a 2-oxa-5-thiabicyclo[4.1.0]heptane derivative, $C_7H_{10}Cl_2O_3S$, (I), and a 2*H*,3*H*,5*H*-1,4-dithiepine derivative, $C_7H_9ClO_4S_2$, (II), are reported. The six-membered ring in (I) has an envelope conformation and the seven-membered ring in (II) adopts a chair conformation. There are no untoward intermolecular interactions in (I), but two Cl atoms make a short intermolecular contact across an inversion centre in (II), with a Cl$\cdots$Cl distance of 3.2784 (9) Å, some 0.22 Å less than the sum of the van der Waals radii.

Comment

The reaction of dichlorocarbene with a 2,3-dihydro-1,4-oxathiine gives rise to a 2-oxa-5-thiabicyclo[4.1.0]heptane, a heterocyclic system whose structure has not been described previously. By contrast, the same reaction with a 2,3-dihydro-1,4-dithiine gives a 2*H*,3*H*,5*H*-1,4-dithiepine, a system not previously made by the ring expansion of a six-membered heterocycle (Brewer & Znotins, 1996). In view of the novelty of the above bicycloheptane system and the fact that no X-ray analysis of a 2*H*,3*H*,5*H*-1,4-dithiepine has yet been published, it was felt worthwhile to examine the structure of suitably crystalline examples of each type of compound. Details of the structures of the title compounds, *i.e.* the 5,5-dioxide, (I), and 1,1,4,4-tetraoxide, (II), are provided here.



(I)



(II)

The six-membered ring in (I) has an envelope conformation with C3 at the flap and the seven-membered ring in (II) adopts a chair conformation. In both compounds, molecular dimensions are normal. There are no untoward intermolecular interactions in (I), but two Cl atoms make a short intermolecular contact across an inversion centre in (II), with a $Cl6\cdots Cl6^{i}$ distance of 3.2784 (9) Å [symmetry code: (i) $2 - x$, $2 - y$, $1 - z$], some 0.22 Å less than the sum of the van der Waals radii.

Experimental

The syntheses of 7,7-dichloro-1,6-dimethyl-2-oxa-5-thiabicyclo[4.1.0]heptane and 6-chloro-2,3-dihydro-7-methyl-5-methylene-2*H*,3*H*,5*H*-1,4-dithiepine have been described previously (Brewer & Znotins, 1996). Both compounds are somewhat unstable oils; however, oxidation with 40% peracetic acid gave the corresponding 5,5-dioxide, (I), and 1,1,4,4-tetraoxide, (II), derivatives, which are both stable crystalline solids suitable for X-ray analyses. The bicycloheptane (I) was recrystallized from ethanol to give white crystalline plates (m.p. 406–420 K); the dithiepine tetraoxide (II) was recrystallized from ethyl acetate giving chunky white needles from which a suitable crystal was cut (m.p. 439–447 K).

Compound (I)

Crystal data

$C_7H_{10}Cl_2O_3S$
$M_r = 245.11$
Monoclinic, $P2_1/a$
$a = 11.2341$ (17) Å
$b = 6.8536$ (11) Å
$c = 13.0566$ (12) Å
$\beta = 97.307$ (9)°
$V = 997.1$ (2) Å^3
$Z = 4$

$D_x = 1.633$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 9.45$–15.75°
$\mu = 0.831$ mm^{-1}
$T = 294$ (1) K
Plate, white
0.35 × 0.35 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{\min} = 0.762$, $T_{\max} = 0.931$
2267 measured reflections
2166 independent reflections
1718 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.008$
$\theta_{\max} = 26.96°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity variation: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.075$
$S = 1.063$
2166 reflections
120 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.3140P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

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

C1—O2	1.394 (2)	S5—O51	1.4313 (16)
O2—C3	1.432 (2)	C7—Cl71	1.7428 (18)
C4—S5	1.770 (2)	C7—Cl72	1.7509 (17)

C1—O2—C3	114.58 (14)	O52—S5—C4	111.28 (11)
O51—S5—O52	117.84 (10)	O52—S5—C6	109.54 (9)
O51—S5—C4	107.26 (11)	C4—S5—C6	104.75 (9)
O51—S5—C6	105.25 (9)	Cl71—C7—Cl72	110.21 (9)

Compound (II)

Crystal data

$C_7H_9ClO_4S_2$
$M_r = 256.71$
Triclinic, $P\overline{1}$
$a = 8.0689$ (8) Å
$b = 8.1209$ (10) Å
$c = 9.9329$ (14) Å
$\alpha = 92.010$ (11)°
$\beta = 110.855$ (11)°
$\gamma = 119.210$ (11)°
$V = 513.19$ (11) Å^3

$Z = 2$
$D_x = 1.661$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.90$–15.05°
$\mu = 0.763$ mm^{-1}
$T = 294$ (1) K
Needle, white
0.39 × 0.25 × 0.19 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{\min} = 0.745$, $T_{\max} = 0.867$
2234 measured reflections
2234 independent reflections

2060 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 26.97°$
$h = -10 \rightarrow 8$
$k = 0 \rightarrow 10$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity variation: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.076$
$S = 1.066$
2234 reflections
130 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.2955P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.017 (3)

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

S1—O11	1.4323 (14)	S4—O42	1.4322 (14)
S1—O12	1.4310 (14)	S4—C5	1.7773 (18)
S1—C2	1.7817 (17)	C5—C51	1.316 (3)
S1—C7	1.7829 (16)	C5—C6	1.481 (2)
C3—S4	1.7704 (19)	C6—C7	1.332 (2)
S4—O41	1.4320 (14)	C6—Cl6	1.7338 (17)
O11—S1—O12	118.22 (10)	O41—S4—C3	106.53 (9)
O11—S1—C2	107.38 (9)	O42—S4—C3	108.93 (9)
O11—S1—C7	107.22 (9)	O41—S4—C5	108.62 (9)
O12—S1—C2	108.41 (8)	O42—S4—C5	106.21 (8)
O12—S1—C7	109.86 (8)	C3—S4—C5	106.64 (8)
C2—S1—C7	104.94 (8)	S4—C5—C6	116.44 (12)
O41—S4—O42	119.29 (9)	S4—C5—C51	118.18 (16)

Molecule (I) crystallized in the monoclinic system; space group $P2_1/a$ from the systematic absences. Molecule (II) crystallized in the triclinic system; space group $P\overline{1}$ assumed and confirmed by the analysis. The H atoms in both (I) and (II) were allowed for as riding atoms (C—H 0.93–0.97 Å). In (II), it was clear from difference maps that the methyl H atoms on C71 were disordered unequally over two orientations (in each case, one C—C—H group was oriented almost normal to the associated ring plane). Refinement of tied occupancy parameters for the two orientations led to values of 0.62 (3) and 0.38 (3). In (I), difference maps showed that there was no disorder of any methyl H atoms.

For both compounds, data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software* (Enraf–Nonius, 1992); data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *NRCVAX*96, *SHELXL*97, *PLATON* (Spek, 2000) and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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References

Brewer, A. D. & Znotins, A. A. (1996). *J. Heterocycl. Chem.* **33**, 217–219.

Enraf–Nonius (1992). *CAD*-4-*PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1998). *PREP*8. University of Guelph, Canada.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2000). *PLATON*. Version of January 2000. University of Utrecht, The Netherlands.

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